Biodiesel properties and automotive system compatibility issues

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ABSTRACT

Acceptability of biodiesel by automotive sector is limited due to some of its adverse properties such as cold flow properties, oxidation stability and corrosiveness with automotive fuel system materials. Adverse cold flow properties of biodiesel lead to the problem of plugging and gumming of filters and injectors. There is a concern about the poor oxidation stability of biodiesel, which results in the formation of sediments and gums causing problem in the engine fuel injection system. Biodiesel reacts with automotive fuel system materials adversely resulting in corrosion of metals and degradation of elastomers. Beside these adverse issues, biodiesel possesses incredible inherent lubricity.

This article aims to review the adverse biodiesel properties like cold flow properties, oxidation stability; corrosive and acidic nature resulting in non-compatibility with automotive fuel system materials. It also discusses the excellent lubrication behaviour of biodiesel and its positive impact. An effort has been made to present the review of 145 research papers along with the sharing of our some in-house experimental results. Additive treatment with biodiesel has been found to be suitable for improving the low temperature properties and oxidation stability. Certain metallic and elastomeric components have been reported as compatible/non-compatible with biodiesel. Although attempts have already been made by some researchers on the adverse properties of biodiesel but the scope is rather limited to the properties alone than correlating the same with automotive materials compatibility.

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Contents

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1. Introduction

The relevance of fossil fuels as an energy resource is now widely acknowledged as unsustainable due to exhausting resources and involvement of these fuels in the contamination of the environment [1]. According to International Energy Agency (IEA) report, the world's primary energy demand is proposed to increase by 55% between 2005 and 2030, at an average annual rate of 1.8% per year [2]. If this trend continues, the world will encounter a huge energy crisis. Hence, to resolve these important issues systematically, renewable and carbon neutral biodiesel is essential for environmental and economic sustainability. Biodiesel covers a range of alternative fuels which can be obtained from plant seeds and vegetable oils as well as animal fats.

Besides the major fascinating energy resource, biodiesel is tending to start-up and performance problems when vehicles and fuel systems are subjected to cold climatic temperatures. In winter season, crystallization of high melting saturated fatty acid methyl esters may cause the plugging of filters and fuel tubes [3–5]. Clogging of filter takes place when the temperature falls below the solidification point of biodiesel [6]. The use of biodiesel and its higher blend is restricted due to their poor cold weather performances [7–9]. While most of the characteristics of biodiesel are comparable to fossil based diesel fuel, improvement of its low temperature, flow characteristics still remain one of the major challenges when using biodiesel as a substitute fuel for compression ignition (CI) engines [10].

Moreover, biodiesel is more susceptible to oxidative degradation than fossil diesel fuel. Industries that transport and store biodiesel, hence, are concerned that biodiesel may form sediment and gum during storage. Also, the diesel engine vehicle and equipment operators require a guarantee that sediments and gum will not form during use. Retaining the quality of new fuel formulations such as biodiesel for extensive use as an alternate fuel for application ranging from on and off road diesel engines to locomotives, stationary power, heat generation and aviation, will depend on improvement of technologies to improve its long term storage stability. Biodiesel stability includes oxidation, storage and thermal stability, but usually termed as oxidation stability. The oxidation instability leads to the formation of peroxide or hydroperoxides molecules [11]. The poor oxidation stability of biodiesel increases the peroxide value, viscosity, iodine value; acid number and gum deposits [12]. These bad effects of biodiesel caused a problem in the engine like damage to the fuel delivery system, filter plugging, injector cocking, corrosion, fusion of moving components, hardening of elastomeric components and engine deposits

[13–15]. The European standards (EN 14112) for oxidation stability propose a minimum value of 6 h induction period at 110 °C, determined by Rancimat induction apparatus [16]. Many studies have revealed that biodiesel possesses a lower induction period than that proposed by the standards.

Furthermore, biodiesel generally experiences degradation of automotive materials resulting in decrease in life of fuel system components [15,17,18]. Biodiesel is more corrosive than fossil diesel [19]. The blends of biodiesel showed corrosion effect on copperish metals [20]. Also, biodiesel have splendid solvent properties [21]. Hence, any deposits in the filters and in the delivery systems may be dissolved by biodiesel and petroleum diesel forms deposits in a vehicular fuel system. As biodiesel can loosen those deposits, they can migrate and clog fuel lines and filters, resulting in the replacement of the filters. Also, biodiesel will react with some elastomers and metals in a destructive way affecting the engine durability problems like injector cocking, piston ring sticking and severe engine deposits [22–24].

The major obstacle in commercialization of biodiesel is high feedstock cost. In European countries biodiesel is being sold at prices economical compared with petroleum diesel fuel because of the tax benefits given by the government to improve the prospective use of biodiesel in various applications. Due to the lack of such tax relief in other countries, the cost of the biodiesel is very high compared to the petroleum diesel. Therefore, various nonfuel applications of biodiesel must be examined. The advent of ultra-low sulphur diesel fuel ($<$ 15 ppm sulphur in US and $<$ 10 ppm in Europe) has raised concern over the ability of these fuels to sufficiently lubricate diesel engine components in the fuel injection system [25]. One of the most promising alternatives for biodiesel application is its use as a diesel fuel lubricity additive [26]. Due to its incredible inherent lubrication properties, biodiesel is utilized as an additive to improve the lubrication properties of conventional fuels. Such usefulness was also accounted for even lower ($<$ 1%) blend level or higher [27–29].

Though some attempts have already been made by researchers to present a review of some biodiesel issues, but the review exploring the biodiesel properties and its effect on engine system compatibility is rather limited. Therefore, the aim of this article is to present a review of adverse biodiesel properties such as cold flow behaviour, oxidation stability, etc. and its effect on automotive system compatibility. Fig. 1 shows elements considered in literature review. After the introduction, the cold flow behaviour of biodiesel, which has importance in low temperature, is reviewed. This is followed by a section that presents a review of oxidation stability. Further, section presents review on the compatibility
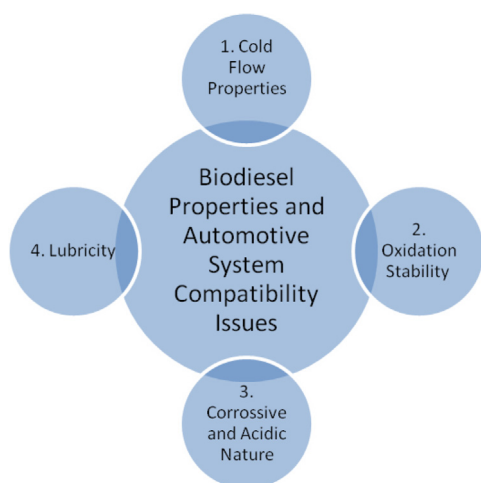
Fig. 1. Biodiesel properties and automotive system compatibility.

of automotive materials with biodiesel. The next section presents reviews of the nonfuel application of biodiesel as a lubricity additive. Finally, summary and conclusion based on the review are presented.

2. Cold flow and system compatibility

Biodiesel development technology is limited due to its poor cold flow behaviour [30]. Crystallization of the saturated fatty acid methyl ester components of biodiesel in cold weather causes fuel starvation and operability problems as solidified material clog fuel lines and filters. With decreasing temperature more solids are formed and material approaches the pour point, the lowest temperature at which it will cease to flow. It has been well recognized that the existence of higher amount of saturated components increases the cloud point and pour point of biodiesel. The cloud point, which generally occurs at a higher temperature than the pour point, is the temperature at which a liquid fatty material becomes cloudy due to the formation of crystals and solidification of saturates. Moreover, a fuel suitable for low ambient temperature must have lowest cold flow properties. There is a relationship between the saturated methyl esters, higher the percentages of saturated compounds the higher the cold flow values [31,32].

The low temperature performance of biodiesel stated that the length of the hydrocarbon chains and the presence of unsaturated structures considerably influence the low temperature flow properties of biodiesel and its higher blend. Kim et al. [33] examined the cold flow performance of biodiesel blends in a passenger car and a light duty truck at −16 °C and −20 °C in the cold chamber. The biodiesel used were soybean oil, waste cooking oil, rapeseed oil, cottonseed oil, palm oil and jatropha oil with different volume ratios (B5, B10 and B20). The cold flow properties like CFPP and cloud point (CP) had an effect on the startability and driveability of both passenger car and the light duty truck. The startability and driveability of a passenger car was good at −20 °C. Off the biodiesel blends examined on light duty truck, the palm biodiesel blend B10 and B20 failed at −20 °C and −16 °C respectively.

Biodiesel attains the cloud point at the start of crystal formation and solidification of saturated components during cooling. Pour point occurs during further cooling as a result of crystal growth and agglomeration involving, not only the saturated, but also unsaturated components. The higher the proportion of saturated components, higher the cloud point and pour point [8]. Moreover, very small (trace) concentrations of minor constituents are identified to affect low-temperature flow performance of biodiesel. These minor

constituents are often referred to as contaminants, though many of them originate either in the parent oil or may be present in the conversion of oil into biodiesel [34].

Currently, a survey for the quality of biodiesel blend in the United States has been conducted in the winter of 2009–2010 by Alleman et al. [35]. In this survey, 40 B6–B20 blended samples from various states were collected and analysed for various vital characterizations as per standard. Few samples failed in induction period stability test while almost all samples showed adequate cloud point, cold filter plugging point (CFPP).The CFPP is defined as the minimum temperature at which a fuel causes a filter to plug due to its crystallization or gelation. Pour point of biodiesel and its blend with different additives can be measured by using the piezoelectric quartz crystal method. Verissimo et al. [36] reported that use of the piezoelectric quartz crystal method is an alternative, precise and easy method to determine the pour point of biodiesel in comparison with the ASTM D97 method. Also, DSC (Differential Scanning Calorimetry) can be employed to determine the pour point of biodiesel.

2.1. Biodiesel production methods and cold flow

It is observed that biodiesel production methods are related with cold flow properties. Kleinova et al. [37] studied the cold flow influence of neat esters of branched chain alcohols with fatty acids and blends of these esters with fossil diesel fuel. This study revealed that the blending of branched chain alcohols up to 10 vol% does not significantly change the cold flow behaviour of petrodiesel. Furthermore, alkoxylation of the unsaturated fraction of biodiesel proposed the prospective benefit of reduced cloud point without compromising with the ignition quality and oxidation stability. Smith et al. [38] synthesized the biodiesel from canola oil by alkoxylation. It was found that cloud point and pour point of methyl and ethyl biodiesel increased slightly while a reduction in 1 °C was achieved for butyl biodiesel.

Li and Shen [7] prepared biodiesel from the common vegetable oils (cottonseed, sunflower, soybean, peanut, corn oil) by transesterification (synthetical biodiesel) and the catalytic cracking method and analysed it for solidification point, CFPP and viscosity as per ASTM standards. The results showed that the pour point of transesterified biodiesel increases considerably while CFPP is lowered as compared to catalytic cracking biodiesel. Also, viscosity of catalytic cracking biodiesel reduced up to 91% as compared to feedstock oil. This study presented that cold temperature behaviour of biodiesel and its blend not only depends on the composition of feedstock oil but also on the production conditions and kind of catalyst used.

Researchers found that the cold flow and storage stability characteristics of FAME based biodiesel can be upgraded by using the thermal cracking method. Seames et al. [39] upgraded the cold flow and storage stability characteristics of soy methyl ester and canola methyl ester in batch cracking reactor (above 400 °C). It was observed that cloud and pour points were decreased to around 20 °C and 15 °C respectively. Also, the stability of fuel was boosted by converting all of the unsaturated esters into lower molecular weight saturated esters.

Dunn [34] focused on the very small (trace) concentration of minor constituents such as saturated monoacylglycerols or free steryl glucosides retained in transesterification. These retained constituents form solid residues when stored during cold season and further settling of these solid residues were found to clog fuel filters and dispensers. Moreover, the saturation and unsaturation composition of biodiesel influence cold flow properties. Biodiesel is more prone to solvency effect when stored at low temperature leading to the formation of precipitate which causes serious damage to the diesel fuel system. Tang et al. [40] observed the precipitate in

soy-, cottonseed and poultry fat biodiesel after storage at 4 °C. Based on Fourier transform infrared (FTIR) spectra, and gas chromatography-flame ionization detector (GC-FID) chromatograms, steryl glucosides are the major cause for formation of precipitate in soy based biodiesel; and monoglycerides in poultry fat based biodiesel. However, the precipitate from cottonseed based biodiesel is due to both steryl glucosides and monoglycerides.

Researchers evaluated the effectiveness of different strategies to improve the cold flow properties of biodiesel containing high saturated methyl esters. Study [41] on palm, tallow, chicken and jatropha blended biodiesel samples were found with higher unsaturated methyl esters such as soy and rapeseed biodiesel samples along with cold flow improver. Also, influence of removing minor constituents such as steryl glucosides and monoglycerides from biodiesel sample on CFPP were studied. It was found that blending of biodiesel in biodiesel improved CFPP (Viscoplex 10-305 in 5%), but the removal of minor constituents such as steryl glucosides and monoglycerides from biodiesel sample did not improve the CFPP. However, distillation improved CFPP by 1–3 °C.

2.2. Cold flow improving techniques

In order to overcome the problem of poor cold flow properties of biodiesel at low temperature, the following methods are adopted to improve the cold flow behaviour of biodiesel.

2.2.1. Cold flow improvers/additives

Biodiesel investigators have proposed several approaches to improve the low temperature properties of biodiesel. Schumacher et al. [42] evaluated the use of straight vegetable oil (SVO) additive OS110050 (presently sold as Lubrizol 7671) to improve the cold weather functionality of biodiesel/diesel fuel. Specially, cloud point, pour point and viscosity of methyl esters of soybean (biodiesel) and low sulphur diesel (LSD) were measured. The results showed that addition of SVO additive improved the cloud and pour point of soya methyl ester and its blend with LSD.

Another approach to enhance the cold fluidities of biodiesel is to use cold flow improvers. Chiu et al. [43] investigated the impact of four cold flow improvers namely OS110050, Bio Flow-870; Bio Flow-875 and diesel fuel antigel on biodiesel produced from soybean oil and its mixed blend with various kinds of diesel fuel as per ASTM. It was found that cloud point and pour point were reduced up to −18 °C and −32 °C. Another study by Boshui et al. [44] investigated the effect of cold flow improver namely olefin-ester copolymers (OECP), ethylene vinyl acetate copolymer (EACP) and polymethyl acrylate (PMA) with soybean biodiesel. It was found that OECP significantly reduced pour point and CFPP by 8 °C and 6 °C respectively at the additive content of 0.03%.

Biodiesel and its higher blend are additized to improve the cold flow performance. Bhale et al. [10] explored the cold flow properties of 100% biodiesel produced from Madhuca Indica (Mahua) oil, by using ethanol, kerosene and commercial additive (Lubrizol) as a cold flow improver in blending form and essential properties were measured as per ASTM. The experimental results showed that ethanol and kerosene improved cold flow performance. The effect of 2% Lubrizol is similar to that of 20% ethanol. The reduction in cloud point of mahua methyl ester (MME) was observed from 18 °C to 8 °C when blended with 20% ethanol and 5 °C when blended with 20% kerosene. Similarly the reduction in pour point was noted from 7 °C to −4 °C when blended with 20% ethanol and up to −8 °C when blended with 20% kerosene. The obtained results revealed that the cold flow improvers boosted the low temperature flow characteristics of MME, which may be used as favourable as petrodiesel.

Chastek [45] examined the low temperature flow properties of canola based biodiesel by depression via dilution, dilution in tolune and polymeric additization, etc. It was found that of the 13 polymeric additives, 1% poly (lauric methacrylate) homopolymer effectively improved biodiesel cold flow properties. The pour point and low temperature flow test (LTFT) was depressed as much as 30 °C and 28 °C respectively.

Couple of studies was conducted by Joshi et al. [46,47] to improve cold flow performance of biodiesel by blending and additization. The first study is devoted to investigate the effect of blending ethanol, isopropanol and butanol (5%, 10% and 15%) to improve the low temperature operability of poultry fat methyl ester (PFME). It was found that butanol–PFME blend showed slightly superior low temperature operability as compared to ethanol and isopropanol. In the second study [47], ethyl levulinate (ethyl 4-oxopentanoate) was used as an additive to upgrade the cold flow properties of biodiesel based on cottonseed oil and poultry fat in the concentration of 2%, 5%, 10% and 20% (vol). It was found that cloud point (CP), pour point (PP) and cold filter plugging point (CFPP) were reduced to 5, 4 and 3 °C respectively while other characteristics follow the ASTM standards. Table 1 shows the summary of cold flow performance of biodiesel with additive/improver.

2.2.2. Binary mixtures and blend with diesel

Furthermore, researchers found that blending of biodiesel in biodiesel results in decrease of saturated fatty acids, consequently

Table 1
Summary of cold flow performance of biodiesel with additive/improver.

Biodiesel	Additive /improver	Cloud point (°C)		Pour point (°C)		Reference
		(Before blend)	(After blend)	(Before blend)	(After blend)	
MME	20% ethanol	18	8	7	−4	Bhale et al. [10]
MME	20% Kerosene	18	5	7	−8	
MME	2% Lubrizol	18	8	7	−4	
SFO	1% ozonized SFO	–	–	−5	−24	Soraino et al. [8]
SBO	1% ozonized SFO	–	–	−2	−12	
RSO	1.5% ozonized SFO	–	–	−13	−30	
SME	2% Lubrizol	−4.4	−6.6	−6.7	−17.7	Schumacher et al. [42]
40% SME	2% Lubrizol	−12.2	−15	−15	−17.7	
30% SME	2% Lubrizol	−12.2	−15	−15	−28.8	
20% SME	2% Lubrizol	−15	−15	−20	−31.1	
Canola BD	1% poly (Lauric methacrylate	−12	−12	−16	−46	Chastek [45]
Methyl oleate	1% poly (Lauric methacrylate	−22	−22	−24	−42	
SME	0.03% olefin-ester copolymers (OECP)	–	–	−1	−8	Boshui et al. [44]

SFO=sunflower oil biodiesel; RSO=rapeseed oil biodiesel; MME=mahua methyl ester; CSO=cottonseed oil; PFO=poultry fat oil; SBO=soybean oil biodiesel.

improving cold flow behaviour of biodiesel. Yusup and Khan [48] investigated the blended form of rubber seed oil in palm oil which enhances the cold flow characteristics by reducing saturated fatty acids. In addition, Perez et al. [49] used the bio-oil derived from pine chip (pyrolysis oil) in biodiesel to evaluate the impact of varying mixture on the cold flow characteristics and oxidation stability of resulting mixture by differential scanning calorimetry. The experimental results reported that addition of bio-oil improved the cold flow behaviour and oxidation stability. Zuleta et al. [50] studied binary blend of biodiesel in biodiesel to improve both oxidation stability and cold flow properties. The best biodiesel blend was found at 75% jatropha and 25% castor biodiesel.

Joshi and Pegg [5] explored experimentally and empirically the low temperature flow properties of ethyl esters and its blend derived from fish oil with no. 2 diesel fuel. It was found that as the concentration of diesel in the blend increases the cloud and pour point decreases. Further, this study predicted cold flow properties of biodiesel by empirical equations which estimates close results to that of experimental values. Correlations between CP and fatty acid composition were investigated by Imahara et al. [51]. This correlation was found useful to determine the CP of biodiesel mainly by the amount of saturated esters and it does not depend on the composition of unsaturated esters.

2.2.3. Winterization

Winterization removes the high temperature freezing components by partial crystallization through cooling. Gonzalez Gomez et al. [52] used the winterization technique for waste cooking oil methyl ester (WCOME) to improve the cold flow properties of biodiesel produced from waste cooking oil. The winterization is a simple method in which the biodiesel is cooled slowly to precipitate high melting saturated fatty acid methyl esters. Kerschbaum et al. [4] winterized the biodiesel based on waste cooking oil by micro-heat exchanger to reduce the saturated methyl esters from 21.3% to 9.6%. In this study, the CFPP value was reduced by −9 °C.

The poor performance of biodiesel at low temperature is owing to its long chain saturated compounds, such as C20:0, C22:0 and C24:0. Perez et al. [53] separated these compounds by solvent winterization with methanol to reduce CFPP from 17 °C to −8 °C with a biodiesel loss of 8.93 wt%. The most considerable reduction in pour point was monitored when the biodiesel and additive were obtained from the same source vegetable oil [8].

2.2.4. Ozonization

Ozonization enhances the cold flow properties of biodiesel. Soraino et al. [8] evaluated the ozonized vegetable oils (1–1.5% by weight) as a pour point depressant and reduced the pour point of biodiesel obtained from sunflower oil, soybean oil and rapeseed oil to −24, −12 and −30 °C respectively. It was found that the lowest reduction in pour point was viewed in cases where the biodiesel and the ozonized samples were prepared from the same vegetable oil. This is due to the similarity in the chemical structures of the components of biodiesel and the additives which make greater interaction in their solid phase, leading to a lower pour point. Pour point depressants performed best when the average length of its hydrocarbon chain is the same as that of the main components of the material being treated because of the stronger intermolecular forces of attraction operating along their hydrocarbon chains. In another study, Rafie and Attia [54] evaluated the improvement in pour point by use of (1 wt%) ozonized vegetable oil for neat biodiesel. It was found that the pour point of biodiesel produced from sunflower, linseed oil and mixed oil (soybean, sunflower and oleen oils) was dispersed to 0, −3 and 0 respectively, while ozonized biodiesel showed degradation after 3 weeks storage at room temperature.

2.3. In-house experimental results

Various approaches like blending with fossil based additives, blending with commercial additives and blending biodiesel in biodiesel is studied by present authors. This study showed considerable improvement in cold flow properties and controlled viscosity were observed for biodiesel derived from high free fatty acid oil as shown in Fig. 2. It is observed from Fig. 2, in comparison with ethanol and kerosene, less improvement in cloud and pour point were observed when biodiesel was blended with diesel up to 20%. Compared to ethanol and kerosene, less improvement in cloud and pour point were observed when biodiesel was blended with castor biodiesel and jatropha biodiesel. The effect of 2% commercial additive was found significant compared to other blended materials. The improved low temperature performance of biodiesel (B100) blended with alcohol, fossil based fuels; biodiesel in biodiesel blend; and with commercial antigel additive showed its use under diverse cold climate temperatures.

2.4. Cold flow property and oxidation stability

Cold flow property found dependant on the presence of ester chain length while oxidation stability is found dependent on the presence of polyunsaturated esters [55]. The oxidation stability and low temperature, flow property has a close relationship with major fatty acid components. Park and Kim [15] examined the oxidation stability and CFPP of three kinds of biodiesel blends, palm, rapeseed and soybean. It was found that the CFPP decreased considerably with increase of total unsaturated fatty acid contents. On the other hand, the oxidation stability decreased as the total content of linoleic and linolenic acids increased. Further this study specified empirical correlations to predict the oxidation stability and CFPP, if the composition of the biodiesel blend is known. However, investigators observed that the poor flow properties of biodiesel at cold temperatures are principally because of biodiesel fuel being composed of long-chain with an alcohol molecule attached. If the double bond of unsaturated fatty acids in these long-chain fatty acids could be ruptured selectively, then the cold flow properties of biodiesel fuel would be augmented by reducing its viscosity. Jin et al. [56] studied experimentally the selective hydrothermal oxidation of oleic acid, as a model compound of unsaturated high molecular weight carboxylic acids. Further in this study, the methyl esters used were obtained from the hydrothermal oxidation of oleic acid at different oxygen supply rates. This study revealed that cloud point and pour points of the blend were considerably improved up to −17.5 °C and −30 °C respectively.

Beside this, Wang et al. [57] investigated the use of surfactants (such as sugar esters, silicon oil, polyglycerol ester, diesel conditioner and detergent like chilled sodium dodecylsulfate) fractionation to improve the cold flow characteristics of biodiesel obtained from waste cooking oil. This study reported that surfactants fractionation reduced CFPP from −10 °C to −16 °C by the addition of 0.02% of polyglycerol ester while detergent fractionation reduced CFPP up to −17 °C. In this study, oxidation stability of biodiesel from detergent fractionation was reduced due to increased unsaturation while other parameters remain within standard limit.

To overcome cold flow performance issues, biodiesel obtained from various feedstocks must contain a comparatively high concentration (80–90 wt%) of low-melting point mono-alkyl esters; i.e. biodiesel must possess 80–90 wt% unsaturated long-chain fatty acid alkyl esters. Unsaturated organic compounds are considerably more reactive to oxidation than saturated compounds. With regard to long-chain (C18) fatty acid methyl esters, polyunsaturated esters are approximately twice as reactive to oxidation as monounsaturated esters [58].
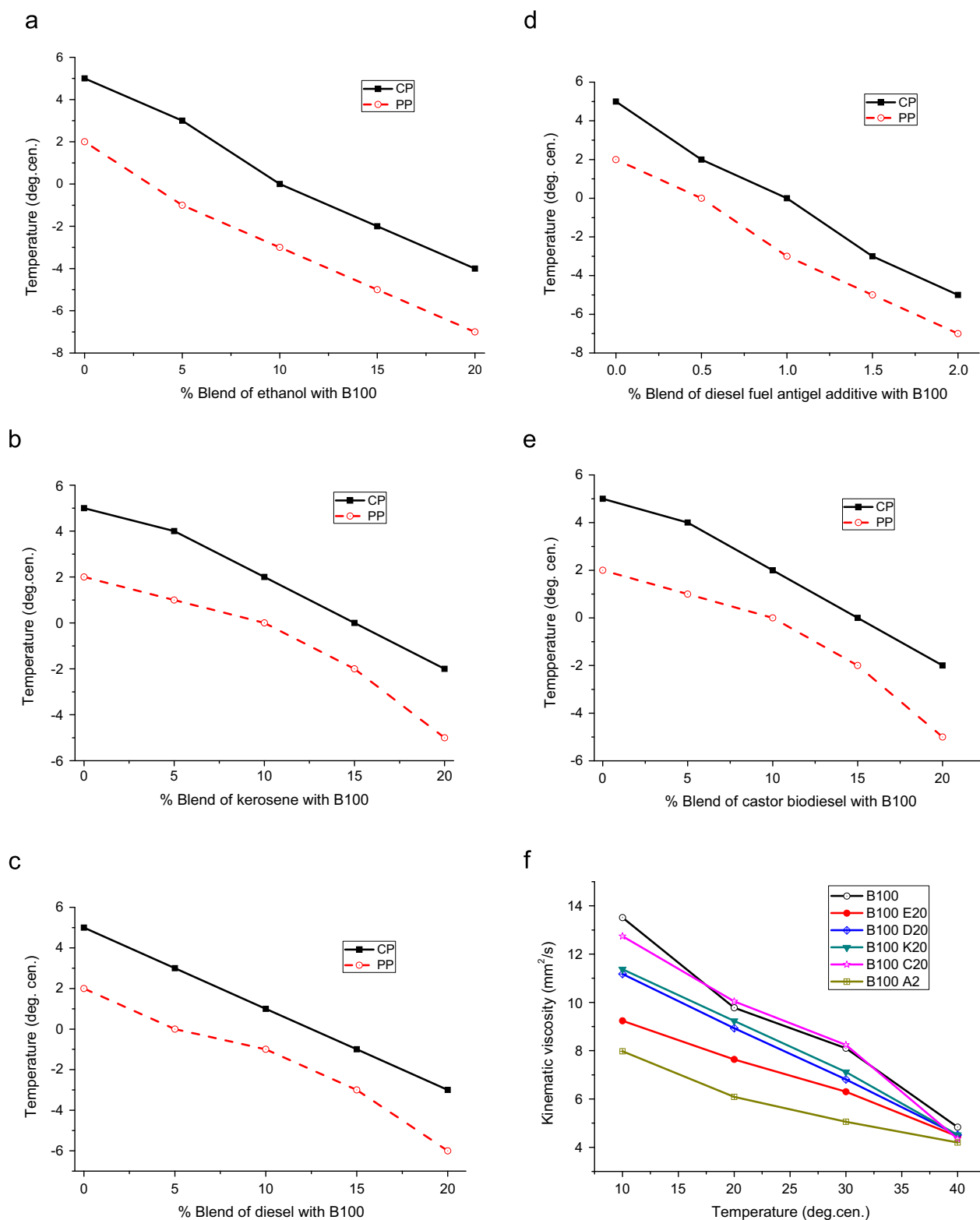
Fig. 2. Effect of ethanol, diesel, kerosene, antigel additive and castor biodiesel on the cold flow properties and kinematic viscosity of biodiesel (B100) in low temperature region. (a) Effect of ethanol on percentage blend of biodiesel, (b) effect of kerosene on percentage blend of biodiesel, (c) effect of diesel on percentage blend of biodiesel, (d) effect of antigel additive on percentage blend of biodiesel, (e) effect of castor biodiesel on percentage blend of biodiesel, (f) effect of ethanol, diesel, kerosene, castor biodiesel and antigel additive on the kinematic viscosity of B100 in low temperature region.

Review done so far on cold flow properties revealed that poor cold flow properties of biodiesel causes engine system operability problem in low temperature region. The low temperature performance of biodiesel showed that the length of the hydrocarbon chains and the presence of unsaturated structures considerably affect the low temperature flow properties of biodiesel. Higher unsaturated compounds are undesirable for good cold flow value. Cold weather performance of biodiesel not only depends on the composition of feedstock oil but also on the production methods and kind of catalyst used. In addition, it was found that biodiesel is

more prone to solvency effect when stored at low temperature. Use of cold flow improver, blending in diesel, binary blending found suitable to improve cold flow values. Some in-house experimental results using these methods showed satisfactory improvement in cold flow properties of biodiesel derived from high FFA feedstock. Ozonization and winterization can be used to improve cold flow of biodiesel. Generally, biodiesel with good oxidation stability showed poor cold flow properties.

3. Oxidation stability and system compatibility

The oxidation process of biodiesel involves three basic steps: initiation, propagation and termination. Firstly, the hydrogen of polyunsaturated fatty acids is simply removed to form carbon based radical (R·), which then reacts with oxygen in propagation reaction to form peroxy radical (ROO·) and a hydroperoxides (ROOH). This peroxide radical generates a new radical in the esters which binds with the oxygen present in the air. At this stage, hydroperoxides level grows fast into the propagation stage. During this auto-oxidation phase, the formation of decomposed by-products occurs at an exponential rate [59,60].

Biodiesel has lower oxidation stability as compared to mineral diesel because biodiesel has high content of unsaturated methyl esters, particularly poly-unsaturated methyl esters which can be simply oxidized as methyl linoleate (C18:2) and methyl linolenate (C18:3), which causes the formation of decomposed compounds such as acids, aldehydes, esters, ketones, peroxides and alcohols. These products not only influence the properties of biodiesel, but also bring about the dilemmas of engine operation [61]. Biodiesel initiated a problem in the engine like damage to the fuel delivery system, filter plugging, injector cocking, corrosion, fusion of moving components, hardening of elastomeric components and engine deposits.

McCormic et al. [14] studied the factors impacting the stability of biodiesel (B100) samples collected as a part of 2004 nationwide fuel quality survey in the United States. Soy, waste oils and tallow samples were collected. The 27 samples were assessed for stability using ASTM D2274 test for insoluble formation and the oxidation stability index (OSI) method (via Rancimat instrument) for induction time. It was found that the polyunsaturated content (or oxidizability) has the highest impact on both increasing insoluble formation and reducing induction time. It was further noted that the formation of insoluble is also measurably decreased by increasing relative antioxidant content and increased by total glycerine content.

It was elucidated that the supercritical methanol method is useful especially for oils/fats that have higher peroxide values [62]. Oxidation stability of biodiesel prepared by the supercritical methanol method was assessed by Xin et al. [63] through the exposure of biodiesel to supercritical methanol at 270 °C/17 MPa for 30 min. Accordingly, it was noted that after the exposure oxidation stability enhanced for biodiesel with initially high in peroxide value, while it was slightly decreased for that with initial low peroxide value, compared with unexposed biodiesel prepared by the alkali-catalyzed method. During supercritical methanol exposure, most hydroperoxides were decomposed due to high temperature and high pressure, while tocopherol stayed almost unchanged in its content for high unsaturated biodiesel (safflower and rapeseed biodiesel) but a little decreased for low unsaturated biodiesel (palm biodiesel).

According to Jain and Sharma [64] Rancimat test (EN 14214, ASTM D6408-08, D5304-06) has been recommended as a significant method to determine the thermal stability of oils, fats and biodiesel fuels. The effect of oxidation stability can be measured by accounting antioxidant concentration, fatty acids and total glycerine content. The experimental result available on the stability of biodiesel is presented in the following section.

3.1. Effect of antioxidants

Oxidation of biodiesel cannot be stopped completely but can be appreciably slowed down by the use of antioxidants, which are chemicals that inhibit the oxidation process [65]. Dunn [58] studied the effect of antioxidants such as tert-butylated hydroxy toluene (BHT), tert-butylated hydroxyanisole (BHA), pyrogallol (PY), propyl galate (PrG) and tert-butyl hydroxyl quinone (TBHQ) on the stability of methyl esters of soybean oil by non-isothermal pressurized-differential scanning calorimetry. Results showed that PrG, BHT and BHA were most effective in increasing oxidation stability and α-Tocopherol was least effective. Biodiesel obtained from rapeseed oil, sunflower oil, used frying oil, and beef tallow, undistilled and distilled was studied by Mittelbach and Schober [66]. The four synthetic antioxidants pyrogallol (PY), propyl gallate (PG), TBHQ, and BHA produced the remarkable improvement in the induction period. These four compounds and the generally used BHT were chosen for further studies at concentrations from 100 to 1000 mg/kg. The induction periods of methyl esters from rapeseed oil, used frying oil, and tallow could be improved significantly with PY, PG, and TBHQ, whereas BHT was not very effective.

Moreover, the stability of karanja oil methyl ester (KOME) was augmented by blending different antioxidants tert-butylated hydroxy toluene (BHT), tert-butylated hydroxyanisole (BHA), pyrogallol (PY), propyl galate (PrG) and tert-butyl hydroxyl quinone (TBHQ). The physicochemical parameters such as peroxide value and viscosity of samples were determined at regular interval of time under 12 different storage conditions with and without antioxidants. The stability of KOME was studied by Das et al. [67]. The study explored that pyrogallol (PY) as antioxidant exhibited excellent enhancement in the oxidation stability of *Karanja* biodiesel i.e. 16 h at a range of 100 ppm while the other antioxidants have a considerably inferior oxidation period.

Oxidation is an exothermic process, and the reaction heat developed makes it feasible to use differential scanning calorimetry (DSC) or differential thermal analysis (DTA) for its study. Perez et al. [49] used the DSC method to study the oxidation stability and cold flow performance of biodiesel blends with petrodiesel. In another study, [68] PY was found the most effective antioxidant by DTA and Rancimat. In this study, the thermo-oxidative behaviour of two kinds of methyl esters, both distilled and undistilled, stabilized and unstabilized were explored by using differential thermal analysis (DTA). For the stabilization, two antioxidants are used: (i) pyrogallol (PY), which is a commonly used and is a cheap product, and (ii) *t*-butylhydroxytoluene (BHT), which is often used in the chemistry of oils/fats. The results noted by DTA are compared with the oxidation stability tests obtained by the Rancimat method under isothermal conditions. Both techniques showed that oxidation stability increases significantly with the blending of antioxidants and that pyrogallol was found to be very efficient.

Biodiesel obtained from free fatty acids (FFAs) exhibited poor oxidation stability (Rancimat 0.2 h). A study conducted by Chen and Luo [69] examined the usefulness of one natural and 10 synthetic antioxidants, including α tocopherol (α-T); butylated-dhydroxyanisole (BHA); butylatedhydroxytoluene (BHT); 2, 5-di-tertbutylhydroquinone (DTBHQ); Ethanox 4740; Ethanox 4760E; 2,2-methylene-bis-(4-methyl-6-tert-butylphenol) (MBMTBP); N, N-di-sec-butyl-p-phenylenediamine (PDA); propyl gallate (PG); pyrogallol (PY); and tertbutyl hydroquinone (TBHQ), at concentrations between 100 and 1000 ppm to improve the oxidation stability of the FFA-based biodiesel. The order of antioxidant usefulness with respect to the oxidation stability of the FFA based biodiesel was PrG > Ethanox 4740 > PG > Ethanox 4760E, etc. The induction period (IP) of the FFA-based biodiesel increased as the antioxidant concentration was increased and decreased at high test temperatures.

The viability of biodiesel obtained from jatropha (*Jatropha curcas*) oil was explored by Chen et al. [70] with respect to the biodiesel blending properties and its oxidation stability with antioxidants. The oxidation stability and cold filter plugging point of the jatropha methyl ester JME-based biodiesel were developed by blending with palm and soybean oil methyl esters respectively. However, at the same time the oxidation stability and cold filter plugging point (CFPP) of the JME-based biodiesel blends cannot satisfy the EN 14214 requirements. In this study, PY (100–250 ppm) with JME was found to be the most effective antioxidant. The antioxidants naturally present in vegetable oils were either neutralized in transesterification process and/or separated during the subsequent purification or separation process. Therefore addition of synthetic antioxidants was required to improve the oxidation stability of croton oil methyl ester (COME). Thermal and oxidation stability of COME were determined by Kivevele et al. [71] using Rancimat and thermogravimetric analysis methods respectively. It was found that oxidation stability of COME did not satisfy the specifications of EN 14214 (6 h). However, the antioxidant treatment effectiveness was found in the order of PY > PG > BHA. Likewise, the comparative efficacy of six antioxidant additives, viz., vitamin E (α-tocopherol), butylatedhydroxyanisole (BHA), pyrogallol (PY), propyl gallate (PG), tert-butylhydroxytoluene (BHT) and tert-butylhydroxyquinone (TBHQ) at varying concentration levels (100 ppm, 500 ppm, 1000 ppm and 1500 ppm) on freshly prepared *T. belerica* biodiesel (TBME) is studied by Chakraborty et al. [72]. To enhance the stability of freshly prepared TBME, as per EN14214, either 100 ppm PY or 100 ppm PG treatment was observed adequate.

Five antioxidants viz. butylatedhydroxytoluene (BHT), tert-butyl hydroquinone (TBHQ), butylatedhydroxyanisole (BHA), propyl gallate (PG), and pyrogallol (PY) were studied by Jain and Sharma [63]. A B30 blend (30% JCB) has been examined for the same purpose. PY is found to be the best antioxidant among all five antioxidants tested. The binary mixture of antioxidant is used to improve oxidation stability by Tang et al. [73]. The antioxidant formulation of TBHQ/BHA was used to maintain and further improve the oxidation stability of soybean oil based (SBO) biodiesel. This binary mixture of antioxidant maintained IP of distilled SBO-based biodiesel stable over a 6 month period. TBHQ was found the most effective antioxidant for SBO-based biodiesel. In another study by Kivevele et al. [74], it was revealed that PY and PG is an effective antioxidant in the moringa oil methyl ester. The summary of performance of antioxidants is presented in Table 2.

3.2. Effects of storage time, temperature and conditions

Researchers found that water content and air exposure are two important factors affecting the degradation of biodiesel. Storage of biodiesel over extended periods may initiate degradation of fuel characteristics that can compromise fuel quality. In the first study, Bouaid et al. [78] investigated the long term storage stability of biodiesel from different vegetable oils; high oleic sunflower oil (HOSO), high and low *Erucic Brassica Carinata* oil (HEBO and LEBO) respectively, and used frying oil (UFO) under different conditions when stored in white (exposed) and amber (not exposed) glass container at room temperature for a period of 30 months. Acid value (AV), peroxide value (PV), viscosity (γ), iodine value (IV), and insoluble impurities (II) were measured at regular intervals as per standards. Results showed that AV, PV, γ, II increases while IV decreases with increasing storage time. It was found that biodiesel samples exposed to daylight showed significant changes in properties after 12 months as compared to not exposed to sunlight samples. In the second study, Bouaid et al. [79] studied the long term (12 months) storage stability of biodiesel from bioethanol and *Brassica carinata*. The results revealed that the acid value, peroxide value, and viscosity, increased while the iodine value decreased

Table 2
Summary of performance of various antioxidants.

Biodiesel	Antioxidant	Concentration (ppm)	IP (h)	Reference
Karanja	PY	100	16	Das et al. [67]
Soybean	PY, TBHQ	100–300	> 6	Ryu [75]
Soybean	TBHQ	1000	> 12	Tang et al. [73]
Pongamia	PY	3000	34	Obadiah et al. [76]
FFA	PY	100	> 6	Chen et al. [69]
JME	PY	100–250	> 6	Chen et al. [69]
COME	PY	200	12	Kivevele et al. [71]
Moringa	PY, PG	200	> 6	Kivevele et al. [74]
TBME	PY, PG	100	6.23	Chakraborty, [72]
JME	TBHQ, BHA	600	> 6	Lamba et al. [77]
JME	PY	100	> 6	Jain and Sharma, [64]

COME=Croton *Megalocarpus* oil Methyl Ester; TBME=*Terminalia belerica* Methyl Ester; JME=Jatropha Methyl Ester.

with increasing storage time of the biodiesel sample. Fatty acid ethyl esters (biodiesel) from *Brassica carinata* oil were very stable because they did not demonstrate a rapid increase in peroxide value, acid value, and viscosity with increasing storage time.

In addition, oxidation stability of methyl esters of safflower stabilized with propyl gallate whose concentration ranges from 0 to 5000 ppm was explored by Xin et al. [80] using the Rancimat method at temperatures from 100 °C to 120 °C. Temperature and concentration of the antioxidant were accounted to act the negative and positive results on the oxidation stability of biodiesel. The results obtained proposed that biodiesel fuel stored at lower temperatures is favourable for long time storage of biodiesel without degradation. It was reported that the induction period of biodiesel increases with the increase of antioxidant concentration and decreases with the increase of temperature.

Storage temperature, storage time, biodiesel blend level, and feedstock affect the mass of precipitate formed at low temperature storage. Tang et al. [40] examined precipitates in soybean oil (SBO), cottonseed oil (CSO), and poultry fat (PF) based biodiesel blends after storage at 4 °C by Fourier transform infrared (FTIR) spectra, and gas chromatography-flame ionization detector (GC-FID) chromatograms. CSO and PF based biodiesel were observed to have a lower mass of precipitates than the SBO-based biodiesel. Besides, different rates of precipitate formation were observed for the B20 versus the B100. These results suggested that the formation of a precipitate during cold temperature storage was dependent on the feedstock and blend concentration. The solvency effects of biodiesel blends were more pronounced at low temperature than at room temperature leading to a higher amount of precipitates formation. It was found that steryl glucosides are the major cause of precipitate formation in SBO-based biodiesel; while for PF-based biodiesel; the precipitates are due to monoglycerides. However, the precipitates from CSO-based biodiesel are due to both steryl glucosides and mono-glycerides.

High temperature storage influences the oxidation behaviour of biodiesel. Lin and Chiu [81] studied the oxidation stability of palm based biodiesel at 20 °C and 60 °C with and without BHT. This study revealed that water content, acid value, kinematic viscosity and peroxide value were found to increase more quickly as storage time elapsed and there was a higher level of oxidative degradation in the biodiesel sample without antioxidant that was stored at higher temperature i.e. at 60 °C. An attempt has been made by Agarwal and Khurana [82] to find the best suitable antioxidant for karanja oil methyl ester stored in different storage conditions. PY was found to be the most effective antioxidant when sample was stored under dark conditions without exposure to light and metallic surfaces.

To make FAME competitive and capable to satisfy the European biodiesel specification, treatment with antioxidants to improve the

oxidative stability is necessary. The effects of the antioxidants (vitamin E, BHA, BHT, TBHQ, and PG) in the concentration of 100–1000 ppm on the storage stability of used frying oil methyl esters (UFOME) were examined by Loh et al. [83] for 5 weeks. The effectiveness of antioxidant with respect to the oxidative stability of UFOME was found: vitamin E < BHT < TBHQ < BHA < PG. Moreover, the effect of long-term storage on the physical properties of poultry fat and its mixtures with No. 2 petroleum diesel fuel was studied by Geller et al. [84]. This work examines dynamic viscosity, specific gravity, sediment accumulation, separation (layering) and corrosive properties. Fuel mixtures of petroleum diesel and increasing poultry fat concentrations of 20%, 40%, 60%, 80% and 100% were stored for 1 year in small scale (1 L), controlled, laboratory conditions (4, 38, 54.4 °C and room temperature) while 20% and 80% biofuel mixtures were also subjected to outdoor ambient conditions in a pilot scale (250 gal) storage study. Monthly measurements of viscosity and specific gravity were recorded. A study of the sedimentation and layering of these fuels was conducted as well as a 10 month corrosion study using corrosion coupons in 20% and 80% biofuel mixtures. Additionally, the effect of antioxidants on these fuels was also studied. It has been shown that antioxidants increase oxidative stability of stored animal fats. This study also required to explore the stabilizing effect of antioxidant on relative fuel properties of stored poultry fat. Antioxidants inhibit the formation of free fatty acids in triglycerides; the effect of this inhibition on significant fuel properties of poultry fat was studied. Corrosive properties of these biofuels were usually as expected; brass and copper were prone to attack by these fuels whereas 316 stainless steel and carbon steel were not. In another study, the corrosion of fuel containers due to oxidation is studied by Boonyongmaneerat et al. [85]. The static immersion (ASTM G31-72) study carried out to investigate the fabrication and use of electrodeposited nickel and nickel–tungsten alloys as potential coating materials that effectively protect steel-based biodiesel containers from corrosion. Pure nickel coating showed high resistance to the corrosive character of biodiesel and its vapours. Besides, the coating displayed minimal catalytic influences on the oxidation of biodiesel.

Oxidation of biodiesel is very susceptible to surface area of contact of biodiesel with air. Increasing surface area accelerated oxidation and affected the fatty acid composition [86]. To get an extremely stable biodiesel and to avoid oxidation, it is necessary to take special safeguard during the storage such as limiting access to oxygen and exposure to light and moisture. However, the viscosity and decomposition of biodiesel linearly increased with the increase of temperature while densities and combustion heat of biodiesel fuels decreased linearly with the increase of temperature [87].

3.3. Effect of metal contamination and deactivator

Biodiesel storage tanks and barrels were made up from different transition metals such as iron, nickel, manganese, cobalt and copper. Sarin et al. [88] studied the influence of metal contaminated (2 ppm) and antioxidant on the oxidative stability of jatropha methyl ester. The oxidation stability of metal contaminated jatropha methyl ester (JME) was found to increase with the increase in dosage of phenolic antioxidant. It was found that minimum 500 ppm dosage of antioxidant was essential to enhance the induction period of iron and nickel contaminated and minimum dosage of 700 ppm of antioxidant in manganese contaminated JME was required to meet EN-14112 specification for biodiesel oxidation stability. Further, for cobalt and copper contaminated JME, minimum dosages of 900 ppm and 1000 ppm respectively were needed. In the second study [89], the cost implication of antioxidant is considered, as antioxidant is an expensive chemical. In this study, the attempt was to increase the oxidation stability of metal contaminated jatropha biodiesel by

doping metal deactivator with antioxidant, with varying concentrations in order to meet the EN-14112 standard required for oxidation stability. It was reported that blending of antioxidant can be reduced by 30–50%, therefore the cost, even if very small amount of metal deactivator is doped in jatropha biodiesel to meet EN-14112 specification.

Jain and Sharma [90] presented the relationship of IP with antioxidant concentration and metal contaminants on the oxidation stability of *Jatropha curcas* biodiesel (JCB), taking pyrogallol as the most efficient antioxidant. This study showed that Cu had the strongest catalytic effect followed by Co, Mn, Ni, and Fe. It was also found that beyond a concentration of 2 mg/L, IP values remained almost constant as concentration of metal is increased. In addition, the correlations obtained in this study can be applied to predict the amount of antioxidants needed.

3.4. Stability with low sulphur diesel blends

A biodiesel storage stability study was carried out by Farahani et al. [91] on ultra-low sulphur diesel fuel (ULSDF) and three biodiesel base stocks (B100) derived from tallow, yellow grease and canola with fuel blends (B2, B5, B10, and B20). The storage stability study consisted of determining and noting the changes in acid number (AN, ASTM D664-04) and kinematic viscosity (ASTM D445) over 10 months with different samples stored at 5 °C, 40 °C, and cyclic thermal conditions. The results revealed that biodiesel blend (from tallow) shows greater stability under accelerated oxidative testing while biodiesel blend (from yellow grease) shows the worst stability. Moreover, it was found that diesel fuel holding catalytically-cracked compounds appeared to be more unstable, compared to hydrotreated straight run diesel fuel. Karavalakis et al. [92] aimed to investigate the storage stability of commercially available biodiesel stabilized with different phenolic antioxidants and blended with a typical automotive low sulphur diesel fuel at proportions of 7, 10 and 20% v/v over a 10 week time. The experimental results revealed that TBHQ, PG and PA were the most efficient additives in neat methyl ester, whereas BHT and BHA were the least useful.

The impact of different antioxidants depends on the different types and quality of biodiesel/diesel blend. Karavalakis and Stournas [93] studied the performance of five antioxidants with biodiesel and blend with low sulphur diesel by the modified Rancimat method (EN 15751). It was indicated that BHT and BHA showed the lowest performance in neat biodiesel whereas their use in biodiesel blend showed greater oxidation stability. PG and PA were found the most effective antioxidant in both neat biodiesel and blended biodiesel. In another study [77], the effect of addition of antioxidant was studied on the Euro III high speed diesel and jatropha biodiesel blends. It was revealed that TBHQ and BHA as the most effective antioxidants.

Dantas et al. [94] investigated the oxidative stability of corn biodiesel, obtained by base-catalyzed transesterification reaction, using the ethanol route, during its long-term storage and heating (150 °C). In this study, thermal analysis techniques, such as TGA and pressure differential scanning calorimeter (PDSC) were used along with UV/vis spectroscopy, physico-chemical parameters and viscosity. The oxidative decomposition was verified with the increase of the dynamic viscosities. PDSC curves confirmed that the oxidation onset temperature was reduced as the sample was exposed to degradation factors during heating and storage. It was demonstrated that UV–vis spectrometry technique is a significant tool to study the oxidative stability of biodiesel. The oxidative stability of lower blends of JCB can be improved by blending with petrodiesel having good oxidation stability, due to lack of unsaturated fatty acids, without adding antioxidants. However, above 20% blend, antioxidants are required to achieve the storage stability.

3.5. Engine performance with antioxidants dosed biodiesel

Engine performance and exhaust emissions in diesel engine were not affected by the addition of antioxidants in biodiesel derived from soybean. Ryu [75] investigated the influence of antioxidants on the oxidation stability of biodiesel fuel, the combustion characteristics and the exhaust emissions of a diesel engine. The results reveal that the efficiency of antioxidants is in the order TBHQ > PrG > BHA > BHT > α-Tocopherol. The oxidative stability of biodiesel fuel achieved the 6-h quality standard with 100 ppm TBHQ and with 300 ppm PrG in biodiesel fuel. Antioxidants had no significant effects on the exhaust emissions of a diesel engine. The brake specific fuel consumption of biodiesel fuel with antioxidants decreased more than that of biodiesel fuel without antioxidants, but no trends were found in proportion to the type or concentration of antioxidant.

In addition to oxidation stability, the effects of antioxidant on engine performance and emission have been presented by Khurana and Agarwal [62]. In this investigation, oxidation stability of biodiesel derived from non-edible feedstocks such as *Neem*, *Karanja* and *Jatropha*, stabilized with anti-oxidant pyrogallol (PY) was studied by DSC. The higher onset temperature was recorded for methyl esters of *Neem* and *Karanja* oil. The higher the onset temperature value the more stable the biodiesel. It was found that stability increases with increasing the dosage of antioxidants. This study results revealed that jatropha biodiesel was more stable compared to *Karanja* and *Neem* by the Rancimat method. However, addition of antioxidant did not affect significantly the performance and emissions.

It was found that biodiesel has lower oxidation stability than diesel. Oxidized products not only attack the properties of biodiesel, but also bring about the problems of engine operation. It is impossible to stop completely oxidation of biodiesel but one can slow down the oxidation process by using antioxidants. Pyrogallol was found the most effective antioxidant with different biodiesels. The antioxidants naturally present in vegetable oils were either neutralized in the transesterification process and/or separated during the subsequent purification or separation process. Therefore, addition of synthetic antioxidants was required to improve the oxidation stability. The binary mixture of antioxidant can be used to improve oxidation stability of biodiesel. It was found that the presence of water and exposure to air are two important factors influencing the degradation of biodiesel. At higher temperature storage, the water content, acid value, kinematic viscosity and peroxide value were found to increase more quickly as storage time elapsed and there was a higher level of oxidative degradation. Oxidation of biodiesel is very vulnerable to surface area of contact of biodiesel with air. Increasing surface area accelerated oxidation and affected the fatty acid composition. Moreover, engine performance and exhaust emissions in diesel engine were not affected by the addition of antioxidants in biodiesel.

4. Corrosiveness, acidic nature and system compatibility

The crucial job of the diesel fuel system is to inject an accurate amount of atomized and pressurized fuel into each engine cylinder at the defined time. The main parts of the diesel engine fuel system coming in contact with diesel/biodiesel are the fuel tank, fuel transfer pump, fuel filters, injection pump, and injection nozzles. Ferrous materials like cast irons, steel and non-ferrous materials like copper and aluminium alloys come in contact with fuel. Elastomers are the most common non-metallic materials used in the fuel systems [95,96]. Fuel flows in touch with these common materials under various conditions and thus causes deterioration and degrades fuel system materials in different manner.

4.1. Parts and materials of automotive fuel systems

The main parts of the diesel fuel system that comes in contact with diesel/biodiesel are the diesel fuel tank, fuel filter, lift pump, plunger pump, priming pump, injection pump and the injection nozzles. Fig. 3 shows a CI engine fuel system with common materials in use. In a basic diesel fuel system, the fuel tank stores the diesel fuel and lines deliver the pressurized fuel around the system. The fuel filter removes abrasive and water particles from fuel. The lift pump lifts the fuel from the tank to the injection pump by creating a pressure difference. The injection pump delivers an accurate amount of fuel under very high pressure (about 70 MPa) to the injectors, along the injector pipes. The injector nozzle atomizes the pressurized fuel and sprays it to the combustion chamber. Leak-off pipes collect and return the surplus fuel from the injecting system to the fuel tank via fuel filter. A detailed study of the various material of construction of different components is of utmost importance to ensure a better performance and life of the engine.

A large variety of metals and non-metals are used as the material of construction for the various components of the fuel system. Among them, common ferrous metals are steel and cast-iron, non-ferrous metals are aluminium and copper alloy while the non-metallic substances basically include elastomers. As biodiesel/diesel flows through the system and interact with these materials under diverse static and dynamic conditions, it causes deterioration and degradation of the fuel system materials.

4.2. Corrosive nature of biodiesel

Corrosion is the gradual degradation of material, usually metal, by chemical reaction with its surroundings. It is well-known that biodiesels are more corrosive than fossil based diesel. Biodiesel has a higher electrical conductivity and is more hygroscopic than conventional diesel fuel. This means that, when stored for a long time, it absorbs more water, which in turn leads to hydrolysis of the ester bonds and thus to the formation of free fatty acids (FFA). Free fatty acid may be present as an outcome of incomplete transesterification reaction. Beside this, auto-oxidation of biodiesel can also augment its corrosive characteristics. The pH value falls and the microbiological activity responsible for degradation increases. With the biotic degradation reactions, the properties of the biodiesel also change; in particular, the corrosion potential at the material–fuel interface increases. The materials, along which fuels are conveyed, especially, can suffer considerable damage due to corrosion. Whereas the corrosion behaviour occurring in relation to fossil fuels has been sufficiently studied and documented, but the systematic studies of biodiesel corrosion are still deficient to a large extent. Owing to the various chemical and physical properties, fossil fuels and biodiesels differently influence the corrosion behaviour at the interface between the material and fuel. Corrosion is one of the topics very relevant to the compatibility of biodiesel with system materials. Corrosion characteristics of biodiesel are significant for long term compatibility of CI engine fuel system parts, and very little information is available on this issue. The present section emphasizes to review the results available in the literature on the compatibility and incompatibility of various types of automotive fuel systems material with biodiesel.

According to Kenneth et al. [97] fuel comes in touch with a wide variety of engine parts including fuel pump, gaskets, fuel injector, filters, fuel liners, bearing, piston, piston rings, etc. Among them, copper alloy based parts like fuel pump; bearing, bushing, etc. are mostly influenced by the fuel. Static immersion test was conducted by Geller et al. [84] at 38 °C for 10 months and observed the corrosion of a number of metals e.g. carbon steel, 316 stainless steel, grey cast iron, copper and admiralty brass in poultry fat–diesel mixture of different composition. They observed that carbon
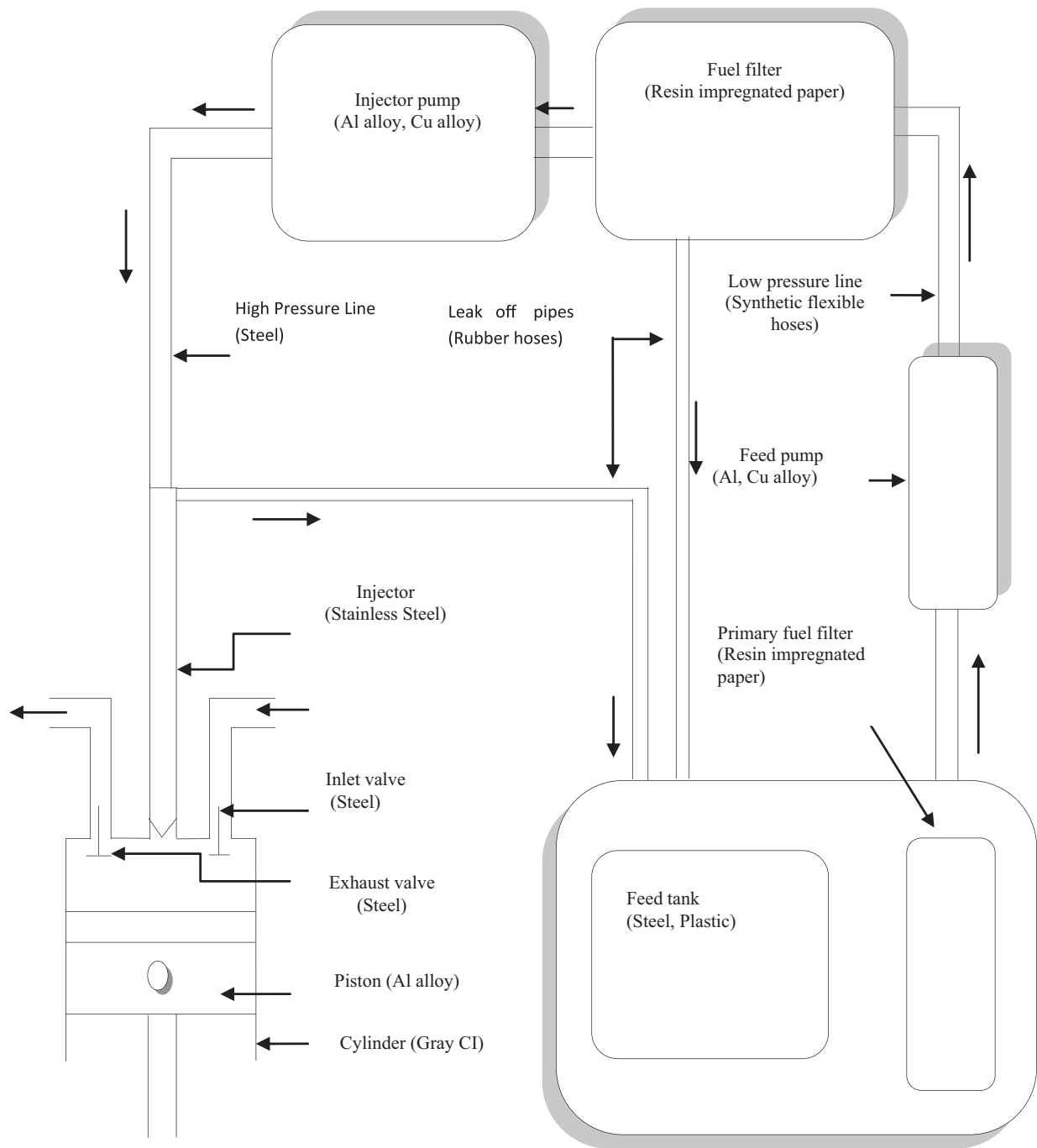
Fig. 3. CI engine fuel systems with common materials in use.

steel and stainless steel did not undergo any weight loss during corrosion tests. Grey cast iron indicated no weight loss in 20% biodiesel but moderate loss in 80% biodiesel. Among the materials studied, copper exhibited maximum weight loss followed by brass. Pitting was recorded in copper and brass. Pitting corrosion was established on sintered bronze filters in oil nozzle after 10 h of operation with biodiesel at 70 °C.

The fact that creates a certain amount of anxiety in researchers that biodiesel degrades through oxidation, moisture absorption, attack by microorganisms, etc. during storage or use and thereby becoming more corrosive. Tsuchiya et al. [98] studied the corrosion of terne sheet steel by immersion in diesel and 5% fatty acid methyl ester (FAME) blended diesel fuel at 80 °C. After 500 h, it was found that pitting corrosion occurred on the surface of the sample immersed in 5% blended diesel. It was observed that corrosion took place even in 2% biodiesel. It was found that the total acid number (TAN) value was not sufficient to describe the corrosive character of biodiesel. According to this study, reformation of extremely corrosive fatty acids takes place from biodiesel during the oxidation process.

Static immersion test was conducted by Kaul et al. [99] for 300 days at 15–40 °C to study corrosion on piston metal and piston liner metal by using diesel and biodiesel derived from *Jathropa curcas*, *Pongamia glabra* (Karanja), *Madhuca indica* (Mahua), *Salvadora oleoides* (Pilu). It was found that higher corrosion occurred in both salvadora and *Jathropa curcas* as compared with diesel. Corrosion in other biodiesel was similar to that in diesel. It was shown that liner metal was more significantly influenced than

piston metal. Study showed that aluminium alloy experienced more corrosion resistance in all the biodiesel tested. However, the corrosion rates of both metals were found to be within acceptable limit.

Investigation was carried out by Haseeb et al. [100] for corrosion behaviour of copper and leaded bronze in palm biodiesel. It was observed that in biodiesel, copper was more vulnerable to corrosion than leaded bronze. It was observed that fresh biodiesel found less corrosive than oxidized biodiesel. For both diesel and biodiesel, corrosion rate of each metal is comparatively higher at 60 °C than at room temperature. The corrosive effect of biodiesel on sintered bronze filter of an oil nozzle was studied by Sgroi et al. [101]. It was found that pitting corrosion occurred on bronze when the nozzle operated at 70 °C for several hours. Corrosive character of biodiesel seems to be due to its FFA elements and impurities remaining after the transesterification process. Results showed that increasing biodiesel concentration in blend increases corrosion of metals. Norouzi et al. [102] carried out static immersion test of rapeseed methyl ester (0%, 50%, 75% and 100%) at 60 °C for 600 h. Copper was more corroded compared with aluminium.

According to Kaul et al. [99] and Maru et al. [103] corrosive nature of biodiesel also depends on its feedstock. The corrosion of pure aluminium in canola based biodiesel by electrochemical technique was studied by Diaz-Ballote et al. [104]. It was observed that the corrosion rate of aluminium strongly depended on the level of impurities in the biodiesel that has been derived from the transesterification process. Water wash used in biodiesel neutralization reduces the corrosion rate significantly. Even lower blend of biodiesel corrodes copperish metals [20]. According to Fazal et al. [105], the rate of corrosion, in both diesel and biodiesel for mild steel, increases with increase in temperature. Beside this, biodiesel is hygroscopic in nature and can absorb moisture from air and thereby can increase the water content [84]. The corrosiveness of biodiesel can be reduced by using additives [98]. It has been reported [106] that copper, brass; bronze, lead, tin and zinc are corroded by biodiesel. These elements accelerate oxidation of biodiesel and hence should be avoided in the fuel system. Conversely, stainless steel, carbon steel and aluminium have been recommended to apply with biodiesel.

According to the review, it can be stated that biodiesel is more corrosive nature than diesel. Generally, static immersion tests were conducted to study corrosive nature of biodiesel. As the concentration of biodiesel in the blend increases, the corrosive nature of biodiesel also increases. Copper alloys are more affected by corrosion than ferrous alloys and aluminium alloys hence should be avoided to use with biodiesel. Lead alloys on terne steel sheet are also affected by biodiesel. The corrosive nature of biodiesel is increased with the increase in the presence of impurities and water. The indicators of corrosiveness namely copper strip corrosion and total acid number found less effective.

4.3. Effect of biodiesel composition on elastomers

The majority of elastomeric components use synthetic rubber compounds, the main reason for using rubber being its inherent elasticity due to shape of rubber molecule. Application of renewable fuels and changes in fuel composition often create many troubles in gaskets, seals, elastomers and O-rings in the engine fuel system. In a CI engine fuel system, fuel comes in touch with different elastomeric components. The compatibility of automotive fuel system components like seals, gaskets and hose materials using conventional fossil based diesel has long been recognized [103,106]. However there is limited literature available on the compatibility or incompatibility of elastomeric engine components with biodiesel. Due to different chemical structures of biodiesel it has consequent different effects on elastomers. Biodiesel is a mixture of alkyl esters while diesel is a mixture of hydrocarbons [84]. Moreover, biodiesel is more prone to oxidation when exposed to air as well as various storage conditions. Also, the biodiesel possesses unsaturated fatty acids. Alkyl esters, the main components of biodiesel can also be hydrolysed in the presence of water to form carboxylic faction. Besides, glycerine is hygroscopic in nature. Curing agent and grade of rubber also affects the characteristics of fuel system elastomers. All these various products including chemical composition of biodiesel affect the chemical and physical properties of elastomers and cause to degrade it [107].

Typically low pressure fuel lines in CI engine are made from synthetic rubber flexible hoses and high pressure fuel lines from steel. Gaskets are made from gasket paper. The commonly used rubber components are nitrile rubber (NBR), hydrogenated nitrile rubber (HNBR), polyvinyl chloride (PVC), acrylic rubber, co-polymer FKM, terpolymer FKM, polychloroprene, Fluoroviton A, Buna, ethylene propylene diene monomer (EPDM), chloroprene (CR), synthetic rubber (SR) and poly tetra fluro ethylene (PTFE) or Teflon. Trakarnpruk and Porntangjitlikit [108] conducted immersion tests for up to 1008 h at 100 °C with six types of commonly used elastomers in fuel systems viz. nitrile rubber (NBR), hydrogenated nitrile butadiene rubber (HNBR), NBR/PVC, acrylic rubber, co-polymer fluoroelastomer (FKM), and terpolymer FKM in B10 (palm biodiesel). The physical properties of elastomers after immersion were measured according to ASTM standards. It was observed that volume and mass increased with respect to time for all test samples excluding NBR and NBR/PVC.

Couple of studies are found on the degradation behaviour of different elastomers by Haseeb et al. [109]. In the first study, the degradation behaviour of different elastomers namely ethylene propylene diene monomer (EPDM), silicone rubber (SR), polychloroprene (CR), polytetrafluroethylene (PTFE) and nitrile rubber (NBR) upon exposure to diesel and palm biodiesel was explored. Static immersion tests in B0 (diesel), B10 (10% biodiesel in diesel), B20, B50 and B100 (biodiesel) were conducted at room temperature (25 °C) for 1000 h. Different physical properties like, changes in weight and volume, hardness and tensile strength were accounted at every 250 h of immersion time in palm biodiesel. The results of this analysis showed that, overall sequence of compatible elastomers in palm biodiesel was found to be PTFE > SR > NBR > EPDM > CR.

In the second study, the impact of palm biodiesel on the degradation behaviour of elastomers such as nitrile rubber (NBR), polychloroprene, and fluoro-viton A was studied. Static immersion tests in B0 (diesel), B10 (10% biodiesel in diesel), B100 (biodiesel) were carried out at room temperature (25 °C) and at 50 °C for 500 h. At the end of immersion test, degradation behaviour was investigated by measuring mass, volume, hardness as well as tensile strength and elongation as per ASTM. After immersion, it was observed that tensile strength, elongation and hardness were significantly reduced for both nitrile rubber and polychloroprene while very negligible changes were recorded for fluoro-viton [101]. Elastomer compatibility may also depend on the feedstock used for the production of biodiesel. Frame and McCormick [110] studied the degradation characteristics of elastomers like peroxide-cured nitrile rubber (N1059), nitrile rubber (N674), high aceto-nitrile content rubber (N0497), fluorocarbon filled with carbon black (V747) and fluorocarbon without carbon black (V884) in diesel, diesel blend with 15% ethanol and 20% soybean biodiesel. It was observed that these elastomers were entirely compatible with B20 and diesel fuel but not in 15% ethanol blend.

Another study, [111] investigated the degradation behaviour of elastomers like gasket (for protective cover of camshaft), camshaft seal and crankshaft seal in ultra-low sulphur diesel, B10, B40 and B100 (biodiesel from waste vegetable oil). Immersion tests were conducted at 90 °C for 22 h, 50 °C for 22 h and 50 °C for 164 h. The resulting deterioration of the elastomers is determined by

measuring the changes in properties before and after immersion according to ASTM D471. It was revealed that the three elastomeric materials used were very compatible with mixtures that contained up to 40% biodiesel. Gasket showed less compatibility as compared to seals but it had the best performance in pure biodiesel.

The effect of exposure to methyl soyester and diesel blends on the tensile strength, elongation, hardness and swelling of several common elastomers was reported by Bessee and Fey [112]. It was reported that nitrile rubber, nylon 6/6, and high-density polypropylene all showed changes in physical properties whereas Teflon, viton 401C and viton GFLT remain unchanged. Celik et al. [113] explored the influences of palm, soybean, sunflower and canola biodiesel on the tractor engine fuel system parts and engine components at real time and long term conditions. It was revealed that if the biodiesel is to be used, elastomeric fuel pipes should be replaced to metal ones due to their hardening problem. According to Hu et al. [20] FKM can be preferred to be used as elastomeric components directly contacted with pure waste oil based biodiesel and their blends. Summary of compatibility of different elastomers with biodiesel is presented in Table 3.

The available literature proposed that fluorocarbon (e.g. Polytetrafluroethylene), acetol, etc. are compatible elastomers with biodiesel. Ethylene propylene diene monomer (EPDM), viton etc. can also be used depending upon different applications. Conversely, few common types of elastomers like nitrile rubber NBR, choloroprene; SBR, neoprene, etc. are found to be incompatible for use with biodiesel. The degradation characteristic of different elastomers with biodiesels from edible, non-edible sources of feedstock is not well understood hitherto. Biodiesel composition including extremely unsteady free fatty acids (FFA) as well as monoglycerides, diglycerides and triglycerides, esters, carboxylic group, methanol and glycerol may have immense impact on elastomer degradation which needs further systematic and comprehensive research.

4.4. In-house experimental results of static immersion test

Although few attempts have already been made by some researchers on the degradation nature of elastomers in biodiesel from palm, rapeseed, etc., but very limited work is available on the degradation behaviour of elastomers in biodiesel derived from high FFAs. Moreover, fuels were not changed in many reported studies throughout the immersion time. By considering this, fuels were replaced with fresh fuels weekly as per recommendation specified in SAE standard. Under such conditions, the experimental work was aimed to study the degradation behaviour of elastomers exposed surface in diesel and high FFA based biodiesel at $55 \pm 2\,°C$ for 500 h as per SAE J1748 standard. Comparative weight loss, volume change and physical properties of the elastomers were investigated before and after immersion. The results are presented as follows:

4.4.1. Volume change
In all the three elastomers, in both diesel and biodiesel, an increase in volume was seen after immersion (see Fig. 4). This change in volume was higher in case of biodiesel. This can be explained by diffusion of liquid in the elastomers. This dissolution, or diffusion, in turn, depends upon the dipole–dipole interactions of the liquid and the elastomers. As biodiesel is more polar than diesel, the dipole–dipole interactions for the elastomers in biodiesel is greater than those for diesel, hence the increased volume change in biodiesel. The amount of swelling or volume change depends upon the chemical behaviour of the elastomers.

4.4.2. Tensile strength change
Tensile strength followed the opposite trend as volume change – significant decrease in tensile strength was observed in case of ethylene propylene dyne monomer (EPDM) when compared to nylon and natural rubber (see Fig. 5). Again, the decrease in tensile strength was greater in biodiesel than diesel. The greater reduction of tensile strength of EPDM points out to the higher loss of cross-linking between its polymeric chains while immersed, whereas in case of the other two elastomers, the comparatively lesser reduction in tensile strength may point towards lesser dissolution of curing and cross-linking agents in the fuel.

Experimental data obtained after performing immersion tests on elastomers in biodiesel and diesel show that the effect of fuel on the material varies from sample to sample. The use of high FFA based biodiesel can cause the detrimental effect on EPDM and nylon as shown by mechanical properties. However, natural rubber is least attacked in high FFA based biodiesel. In other words, EPDM and nylon are incompatible with biodiesel, and hence, should be avoided in the engine fuel system. However, natural rubber is compatible with biodiesel and shows very small changes in properties with exposure to the fuel, and hence, it can be used in the engine fuel system.

4.5. In-house experimental results on clogging of biodiesel filter

In house laboratory results showed higher clogging level in fuel filter when the engine was operated with jatropha biodiesel for a period of 512 h. Approximately 40% weight gain was observed with biodiesel fuel filter as compared to diesel fuel filter. Clogged filter with weight gain is shown in Fig. 6. Solvent property of biodiesel results into clogging of fuel filters. Higher head loss and lower discharge were observed in case of biodiesel operated engine filter as compared to that of diesel operated fuel filter.

Table 3
Summary of compatibility of different elastomers with biodiesel.

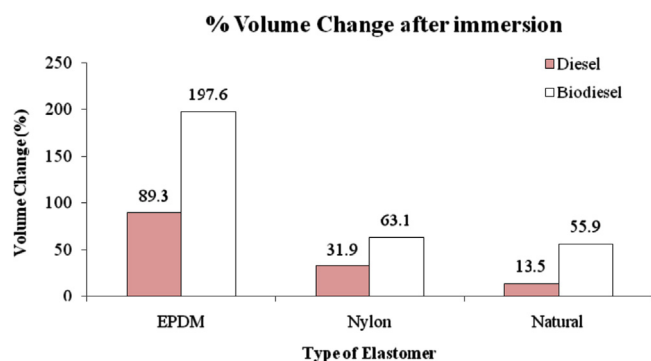| Biodiesel	Elastomers	Compatibility	Reference
Palm	NBR, NBR/PVC	✓	Trakarnpruk and porntangjitlikit
Palm	Hydrogenated nitrile butadiene rubber (HNBR), acrylic rubber, co-polymer fluoroelastomer (FKM), terpolymer FKM	×	[108]
Palm	Polychloroprene (CR), EPDM	×	
Palm	Polychloroprene (CR),NBR	×	Haseeb et al. [109]
Soybean	Nitrile rubber (N1059), nitrile rubber (N674), high aceto-nitrile content rubber (N0497), fluorocarbon filled with carbon black (V747) and fluorocarbon without carbon black (V884)	✓	Frame and McCormick [107]
Methyl soyester	Teflon, viton 401C and viton GFLT	✓	Bessee and Fey [112]
Methyl soyester	Nitrile rubber, nylon 6/6, and high-density polypropylene	×	
Waste cooking oil	FKM	✓	Hu et al. [20]

Fig. 4. Changes of volume of different elastomers after immersion for 500 h at 55 °C.
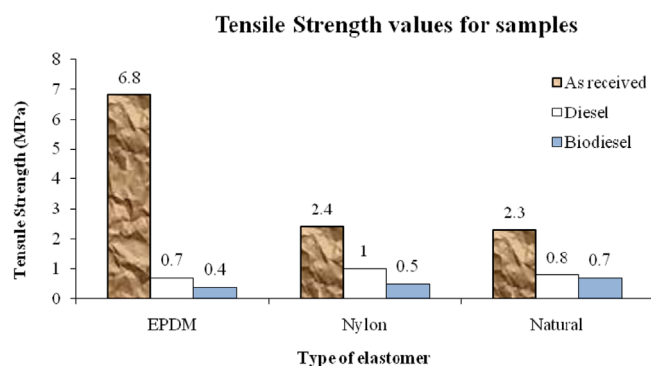

Fig. 5. Tensile strength of different elastomers before and after immersion for 500 h at 55 °C.

5. Lubricity and system compatibility

Now a days biodiesel is being dreamed as a possible extender for petrodiesel. Because of its dazzling lubrication properties, biodiesel can be used as an additive to improve the lubrication properties of petroleum fuels [114]. Researchers devoted to explore the effect of biodiesels obtained from canola, rapeseed, soy, sunflower, poultry fat oil, etc. and different alcohols such as methyl, ethyl, propyl, butyl alcohols and ethers on the lubricity of low sulphur diesel fuel. To search suitable lubricity additive for low sulphur diesel fuel without disturbing exhaust emission norms have become a main objective for the fuel manufacturers. Even though, methyl and ethyl esters are good lubricity improvers, their production methods have their own advantages and disadvantages [115]. In this section, the experimental results available on lubricity of biodiesel and its application as an additive is presented.

To explore the lubricity of esters, Drown et al. [116] analysed four methyl esters and six ethyl esters obtained from different feedstocks for wear measurement by using high frequency reciprocating rig (HFRR). Ethyl ester showed the remarkable improvement compared to methyl ester in the wear properties. Improved lubricity was ascribed to chain length of fatty acids and retained glycerine. Researchers found that, the rate of oleic acid present plays vital role in various properties and parameters of biodiesel. Mozer and Erhan [117] assessed 0.5%, 1% and 2% blend of four synthetic oleochemicals (derived from oleic acid) branched chain ethers against a number of important biodiesel parameters and compared with soy methyl ester (SME). All of the branched chain ethers revealed admirable tribological behaviour (144 μm), oxidation stability and better cold flow performance. This study revealed that branched chain ethers may help in the progress of bio-derived material for the prospective use as an additive. In addition, the wear scar diameter (WSD) and surface roughness was assessed by Sulek et al. [118] to investigate the tribological
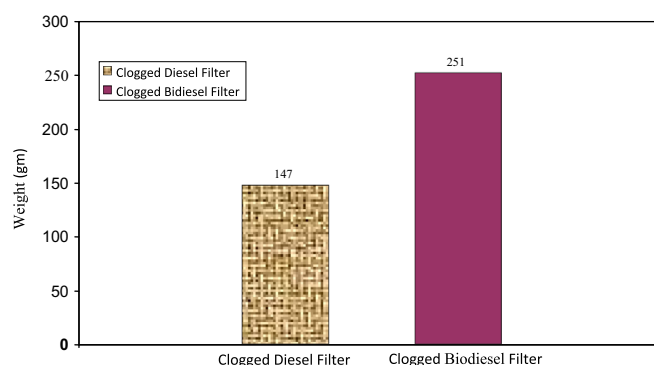

Fig. 6. Weight gain in clogged filters after 512 h of engine operation.

properties of biodiesel produced from rapeseed oil and its blends by HFRR and profilometer. The largest wear scar diameter (WSD) of 310 μm was observed in the case of pure fuel oil. However, WSDs were significantly smaller for composition of rapeseed methyl ester solution. The WSD was 217 μm for pure methyl esters derived from rapeseed oil. Moreover, on measuring the roughness of a metal surface by a profilometer TOPO L50, it was found that under friction conditions the R_A value increased as much as fourfold for fuel oil. The experimental results showed that addition of the esters consistently reduced the R_A values, even by as much as twofold compared to fuel oil. Likewise, the impact of fatty acid esters on lubricity of automotive diesel have closely been examined and reported. However, their impact on lubrication properties of aviation fuel (kerosene) for use in CI engines has been evaluated experimentally by Anastoupoulos et al. [119]. Ten esters of mono-carboxylic fatty acids were tested by HFRR blending in the concentration of 50–2000 ppm. This study reported that all esters ranging from 750 to 1500 ppm were showing wear scar value within the prescribed limit of 460 μm.

The higher contents of contaminants in the biodiesel namely of mono- and di-glycerides, and the presence of sulphur imparts the lubrication behaviour to the biodiesel [120]. Kulkarni and Dalai [26] synthesized canola oil ester using methanol, ethanol and mixtures of methanol/ethanol. These esters were used as a lubricity additive. Lubricity testing of the biodiesel ester was carried out by HFRR using ASTM D6079. It was found that lubricity of ethyl ester was better than that of methyl ester when added 1 vol% to the base fuel. However, the formation of ethyl esters was much slower than the methyl esters. Also, the lubricity of mixed ester (methyl and ethyl) was better than that of pure methyl esters. Moreover, Hu et al. [121] studied the lubrication performance of small quantities of mono-, di- and triglycerides from unrefined biodiesel and refined biodiesel not containing these glycerides by HFRR with diesel as a base fuel. It was found that unrefined biodiesel showed higher lubricity property than refined biodiesels. In addition, methyl esters and mono-glycerides are the main components that determine the lubricity of biodiesel but free fatty acids and diglycerides affected them slightly while triglycerides almost had no effects. In another study, Knothe and Steidley [122] reported that a minimum of two features are required to impart lubricity. These features are polar compounds and shorter carbon chain in esters. In another study, [123] improvement in lubricity of low sulphur diesel was observed by adding 1% v/v of soya based biodiesel with reduction in CO_2 and CO emissions.

However, the tribological properties of coconut oil as an environment friendly lubricant used in 2T engine was investigated by Jayadas et al. [124] and concluded that coconut oil showed higher wear rate compared to commercial lubricants as far as the coefficient of friction is considered. Further, it was found that anti-wear and extreme pressure tribological properties can be improved by

adding suitable anti-wear or extreme pressure additives in coconut oil. Experimental results by Arumugam and Sriram [125] illustrated that the rapeseed oil based bio-lubricant and biodiesel contaminated synthetic lubricant showed better performance in terms of wear and friction.

Hu and Du [121] observed that individual fatty acid esters did not have as remarkable effect on lubricity as did methyl esters obtained from vegetable oils composed of a mixture of several fatty acids. In this view, this study examined the effect of individual component fatty acid methyl esters (FAME) as an additive (0–1%) by HFRR. The obtained results were compared with previous results on lubricity of vegetable oil methyl esters. It was revealed that FAME mixture with high concentration of hydroxylated FAME execute better as lubricity improving agent than that which do not contain a hydroxylated component. With reference to the first study on castor oil it was recommended that its exclusive high level of the hydroxy fatty acids recinoleic acid may impart increased lubricity to the oil and its derivatives as compared to other vegetable oils. Knothe and Steidley [122] was devoted to analyse the success of lubrication behaviour depends on the feedstock and quantity of biodiesel added for diesel fuel and compared their performance to non-hydroxylated methyl esters of other oils such as soy and rapeseed. It was reported that *Lesquerella* oil additive followed castor behaviour closely showing dramatic increase in diesel fuel lubricity at low additive (0.5%) concentration. Furthermore, it was noticed that castor and *Lesquerella* oils are not only both hydroxylated, they are both unsaturated, each having one double bond. Hence, it is suggested that this unique fatty acid profile may impart castor and *Lesquerella* oil methyl esters with excellent values of diesel fuel additives.

Effect of contaminated metals in the oxidation and lubricity of biodiesel is studied by Dodos et al. [126]. It was found that biodiesel sample catalytically oxidized in the presence of copper showed improved lubrication properties in comparison to non-catalytically oxidized sample. Further, it was revealed that BHT, apart from being an antioxidant, could be used as a potential lubricity improver.

5.1. Hydrotreating and low sulphur diesel

Prior to October 1993, the diesel fuel that was sold in the US had a sulphur level of approximately 5000 ppm. In 1993, the Environmental Protection Agency (EPA) mandated that all diesel fuel sold in the US contain 500 ppm or less sulphur. The petroleum refineries, largely due to special hydro-treating of the diesel fuel, produced a cleaner diesel fuel that met this requirement [127]. For metropolitan cities in India, the acceptable limit for sulphur content in diesel fuel was reduced from 500 ppm to 350 ppm by early 2005 and by 2011 it will be further reduced to 50 ppm [128]. On June 1, 2006 the EPA has again lowered the level of sulphur in petroleum diesel fuel. The new standards will be 15 ppm. This reduction in sulphur is projected to reduce diesel engine exhaust emissions by as much as 90% when compared to the 500 ppm low sulphur diesel fuel era. Unfortunately, the hydro-treating that was used to reduce the sulphur produced a fuel that sometimes failed to provide adequate lubrication for the fuel injection system of the diesel engine.

Recently, the initiation of ultra-low sulphur diesel fuel (< 15 ppm sulphur in the US and < 10 ppm in Europe) has raised the concern over the ability of these fuels to adequately lubricate diesel engine components in the fuel injection system [129]. The removal of polar oxygen and nitrogen containing compounds, which occur simultaneously with the removal of sulphur species, is the actual reason for the poor lubricity of low sulphur diesel fuels. Lubricity is the ability of a liquid to provide hydrodynamic and/or boundary lubrication to prevent wear between moving parts. Barbour and Rickard [25]

reported that oxygen definitely contributes to the natural lubricity in diesel fuel, but that nitrogen is a more active lubricity agent than oxygen. It was found that diesel fuels that were high in sulphur but low in nitrogen exhibited poor lubricity. According to Mitchell [130] oxygen and nitrogen have been shown to impart natural lubricity in diesel fuel.

Keith and Conley [131] noted that special hydro-treating, which was used to reduce the sulphur content of diesel fuel, also lowered the lubricity of diesel fuel. They further theorized that the compounds (oxygen and nitrogen) may be rendered ineffective as a result of severe hydro-treatment to desulphurize the fuel. It is important to note that most of the injection systems in diesel engines rely entirely upon diesel fuel to lubricate moving parts that operate with close tolerances under high temperatures and high pressures. Lubricity related wear problems have already been surfaced in Canada, California and Texas when fleets elected to use low sulphur fuels to reduce engine exhaust emissions. Maleque et al. [132] reported that the general esters are considered to show better wear and scuffing behaviour than hydrocarbon based fuels. Also, esters have high affinity towards a metal surface, owing to their polar functional groups and thus form a protective layer on the surface.

5.2. Biodiesel as a lubricity additive in (ultra) low sulphur diesel

Environmental Protection Agency (EPA) mandated that petro-diesel must contain less sulphur to follow the emission norms. Due to stringent emission norms of diesel engines, the sulphur content in new fuel formulation is to be decreased from 5000 ppm (prior to October 1993) to 15 ppm (after June 1, 2006). This new fuel formulation is known as ultra-low sulphur diesel (ULSD) fuel. The crude oil refineries, produced environment friendly diesel by a special process known as hydrotreating. The ULSD reduced exhaust emissions by as much as 90% when compared to 500 ppm low sulphur era. The WSD value of 460 μm was recommended by the European standards in February 1997, and normally accepted by the industry as the least prerequisite for satisfactory field performance. Unluckily, the hydrotreating process failed to impart sufficient fuel lubricity to the fuel injection system of diesel engine as per the standards [133]. The removal of polar oxygen and nitrogen containing compounds, which occur simultaneously with the removal of sulphur species in the hydrotreating process, is the main cause for the poor lubrication properties of low sulphur diesel fuel. Researchers observed that the addition of small quantities (1–2%) of biodiesel with low sulphur (15 ppm) diesel fuel boosted the lubricity to permissible level. The outcome of various studies carried out to find the suitability of biodiesel as an additive in low sulphur diesel is presented as follows:

It was found that the oleic acid present in the biodiesel proposed remarkable effect on the lubricity property of biodiesel. Oguz et al. [134] investigated lubrication performance of 100% biodiesel produced from safflower oil, cottonseed oil, soybean oil and sunflower oil with a pin-on-disc test device under constant load with different sliding velocities. The results obtained were compared with euro diesel (sulphur less than 10 ppm). The experimental results showed that, the coefficient of friction of 100% pure biodiesel was much lower than that of euro diesel. The lowest coefficient of friction in biodiesel was in safflower oil followed by cottonseed oil, soybean oil and sunflower oil. The coefficient of friction obtained at the end of the experiment was the lowest in biodiesel with the highest oleic acid rate. The oleic acid rate of the oils used in the experiment was safflower oil 74%, cottonseed oil 29%, soybean oil 25% and low oleic acidic sunflower oil 19%. The study revealed that the ideal properties of euro diesel can be improved by additizing it with biodiesel.

Munoz et al. [111] used waste vegetable oil biodiesel as an additive in low sulphur diesel fuel in automobile engines. The lubricity of biodiesel and corresponding mixtures with diesel was determined. Among the different standardized tests to evaluate the diesel fuel lubricity, the HFRR (ASTM D6079) method was adopted at different prepared blends to compare wear scars. The wear scar of 600 μm was observed for low sulphur diesel fuel, which is much higher than the maximum value (460 μm) established by European regulation in February 1997. It was observed that when low sulphur diesel includes small percentage of biodiesel, the lubricity gets closer to conventional diesel fuel (wear scar of 283 μm and 312 μm with 10% biodiesel and 5% biodiesel respectively, compared with 314 μm with conventional diesel fuel). Also, 100 ppm biodiesel mixture obtained good lubricating properties, since the wear scar is 338 μm. On adding 10 ppm of biodiesel (B0001) wear scar of 543 μm was obtained (above maximum limit). Thus, the lubricity experiments showed that by including small quantities of biodiesel (5–10%) in the diesel fuel, without a conventional lubricity additive, the lubricating characteristics of the fuel can be obtained as equivalent to diesel fuel (wear scar around 300 μm). Moreover, the study revealed that on incorporating biodiesel in very small quantities (not less than 100 ppm), the wear scar values were within acceptable limit as per EU regulations.

Besides, Arkoudeas et al. [135] assessed the lubricating properties of two low sulphur diesel fuels additized with nine different essential oils such as eucalyptus, lavender, rosemary, pine oil, grape seed oil, kernel peach oil, camomile oil, laurel oil and carrot seed oil. These essential oils were used as lubricating additives with two (A1 and A2 obtained from Greek refinery) low sulphur diesel fuels at the concentration range of 200–5000 ppm. The tribological properties were experimentally determined with HFRR. The results obtained showed that the higher density and viscosity of five out of nine essential oils used i.e. grape seed oil, kernel peach oil, camomile oil, laurel oil and carrot seed oil provide satisfactory mean WSD of less than 460 μm, at the concentration level of 200–5000 ppm, which may be due to their chemical structure characteristics. Moreover, the other four essential oils i.e. eucalyptus, lavender, rosemary, and pine oil could not obtain satisfactory WSD of 460 μm. This study revealed that lubrication mechanism of essential oils may depend on the constituents present and their polar constituent contribution. The summary of lubrication performance of different feedstock, biodiesel and its blends is shown in Table 4.

Lubrication behaviour depends on the feedstock and quantity of biodiesel added. Tobaipaul et al. [136] investigated the lubrication ability of jatropha and palm biodiesel as an additive in ULSD (sulphur less than 6 ppm) fuel by HFRR. It was found that lubricity of biodiesel as an additive varied depending on the source and amount of biodiesel. Moreover, the results obtained showed that jatropha biodiesel is a superior lubricity additive than palm biodiesel due to longer carbon chains of fatty acids in jatropha oil as opposed to palm oil. Experimental study revealed that biodiesel can be used as an additive in ULSD with as little as 0.25–0.5% blends.

The oxygen containing compounds and the mixtures of several fatty acids in methyl esters restored the best lubricating ability to shield the sliding surfaces in fuel injection equipment. However, the existence of oxygen may accelerate the generation of inorganic oxides like Fe_3O_4 which would have positive role in the formation of lubrication film at the contact interface. Sukjit et al. [137] investigated the use of ULSD and fatty acid methyl esters produced from rapeseed methyl ester (RME) blends to improve the lubricity of Swedish diesel fuel MK1 by HFRR. Experimental investigations proved that MK1 has poor lubricity when compared to other base fuels. Among the fuels tested, ULSD verified little improvement. However, a small percentage of RME enhanced lubricity of both the pure MK1 and the blends. Off the various methods of

producing biodiesel, Suarez et al. [138] produced biodiesel from soybean oil by the pyrolysis and alcoholysis method to compare the lubricity of obtained biofuels and their blends with low sulphur (up to 15) diesel and high sulphur (up to 50 ppm) diesel. The biodiesel and its blends were tested for tribological properties by HFRR. Obtained experimental results proposed that biodiesel produced by pyrolysis and alcoholysis can be used as a lubricity additive in low sulphur diesel.

Some studies revealed that on incorporating biodiesel in ultra-low sulphur diesel fuel (without a conventional lubricity additive) in very small quantities (not less than 100 ppm), wear scar values were within acceptable limit as per European regulations. Also, the experimental results proved that, the coefficient of friction of 100% pure biodiesel was much lower than that of euro diesel. Hence, the lubrication properties of euro diesel can be enhanced by additizing it with biodiesel.

5.3. Effect of temperature on lubricity

The different temperature emphasizes different impact on lubricity for different blended fuels. Haseeb et al. [139] investigated the effect of temperature on tribological performance of palm blended biodiesel by using four ball wear machine at temperatures 30, 45, 60 and 75 °C under a normal load of 40 kg for 1 h at speed of 1200 rpm and obtained results were compared with diesel. Results showed that higher blend tends to lower friction coefficient. The WSD increases slightly with increasing temperature. It was found that free water content of the tested fuel increases with increasing temperature while no free water was detected in both diesel and biodiesel in the as received condition. Furthermore, deformation on the surface decreased with increasing the concentration of biodiesel. The study also revealed that friction and wear were increased with increasing temperature. This may be attributed to decreasing viscosity with increasing temperature. At higher temperature, lubricity enhancing film loses its stability due to reduced viscosity and thereby causes increased wear. The effect of temperature on the mixture of ULSD with different biodiesels was studied by Wadumesthrige et al. [140]. It was found that mixture of 2 vol% soya based biodiesel with ULSD showed better lubricity at temperature greater than 70 °C.

5.4. Effects of polar compounds and ethers

The elimination of polar oxygen and nitrogen containing compounds, which occur simultaneously with the elimination of sulphur species in the hydrotreating process, is the major reason for the poor tribological properties of low sulphur diesel fuel. Anastoupoulos et al. [141] investigated the impact of oxygen and nitrogen compounds on the lubrication properties of low sulphur diesel fuel. The oxygen and nitrogen containing compounds were added in low amounts. The influences of 4 specific types of biodiesel, 5 aliphatic amines, 2 tertiary amides, 10 mono-carboxylic acid esters, 3 acetoacetates and 7 esters of dicarboxylic acids with low sulphur diesel fuel were studied experimentally by HFRR. In this study, all types of biodiesel, aliphatic amines and tertiary fatty amides were added in base fuels at the concentration range of 0.05–10%, while the esters of mono- and di-carboxylic acids and the acetoacetates were dissolved in the base fuels at five different concentrations of 50, 100, 500 and 1000 ppm. The available results revealed that all the types of oxygen and nitrogen containing additives augment the lubricity of low sulphur diesel fuel. Wear test conducted by Bhunsoor et al. [142] on linseed oil based biodiesel showed that extra oxygen present in biodiesel fuel will enhance lubricity more than nitrogen and sulphur.

The polar nature of additives plays vital role in the tribological properties when additized with low sulphur diesel fuel. Anastoupoulos et al. [143] investigated the impact of alkyl ethers and alcohols on the tribological properties of low sulphur automotive

Table 4
Summary of lubrication performance of different biodiesels and its blends.

Feedstock	Biodiesel/diesel	Test	Average wear scar diameter (μm)/COF(mm)	Reference
–	Diesel	HFRR	314	Munoz et al. [111]
–	LSD	HFRR	597	
Waste cooking oil	Biodiesel (B100)	HFRR	322	
Waste cooking oil	LSD + 10 ppm BD	HFRR	543	
Waste cooking oil	LSD + 100 ppm BD	HFRR	338	
Waste cooking oil	LSD + BD (5%)	HFRR	312	
Waste cooking oil	LSD + BD (10%)	HFRR	283	
Eucalyptus	5000 ppm	HFRR	581	Arkoudeas et al. [135]
Lavender	5000 ppm	HFRR	535	
Rosemary	5000 ppm	HFRR	532	
Pine oil	5000 ppm	HFRR	534	
Grape seed oil	5000 ppm	HFRR	418	
Kernel peach oil	5000 ppm	HFRR	437	
Camomile oil	5000 ppm	HFRR	418	
Laurel oil	5000 ppm	HFRR	326	
Carrot seed oil	5000 ppm	HFRR	449	
Diesel	100%	HFRR	310	Sulek et al. [118]
Rapeseed methyl esters	100%	HFRR	217	
Oleochemicals	100%	HFRR	144	Mozer and Erhan [117]
SME (soy methyl ester)	100%	HFRR	141	
Safflower oil	100%	Pin on disc	0.8	Oguz et al. [134]
Cottonseed oil		Pin on disc	0.96	
Soybean oil		Pin on disc	1.07	
Sunflower oil		Pin on disc	1.18	
Euro diesel		Pin on disc	1.29	

LSD = low sulphur diesel; BD = biodiesel.

diesel fuel. Seven ethers [i.e. butyl ethyl ether, dibutyl ether, heptyl methyl ether, dipentyl ether, octyl ethyl ether and dioctyl ether] and five alcohols [i.e. octonol, undeconol, tetradeconol, oleyl alcohol and docosanol] were experimented as lubricating additives on two low sulphur diesel fuels, at the concentration range of 50–2000 ppm. All tribological experiments were performed using HFRR test. The lubricating efficiency of the fuels was estimated by measuring the average WSD of the spherical specimen by using a photomicroscope. The results showed that six of seven ethers employed provide satisfactory WSD of less than 0.46 mm, at the concentration range of 750–1500 ppm. Among the ethers of the same molecular type, those having the oxygen in the middle of the molecule appeared to have marginally better lubrication performance for some concentration range. Moreover, the effective concentration was 750 ppm or higher was observed for alcohols. It was revealed that alcohols appeared to be better lubricants than ethers at high concentration, may be due to their more pronounced polar nature.

Literature showed that biodiesel possesses inherent lubricity. Fuel manufacturers are searching for a lubricity additive for low sulphur diesel without disturbing exhaust emission norms. Biodiesel can be used as an additive to improve the lubrication properties of petroleum fuels. Lubrication property depends on the feedstock and quantity of biodiesel added. The higher contents of contaminants in the biodiesel namely of mono- and di-glycerides, and the presence of sulphur imparts the lubrication behaviour to the biodiesel.

5.5. In house experimental results of biodiesel lubricity

Four biodiesel fuels (Pongamia, Jatropha, Mahua and Coconut) were prepared in house using laboratory assembled biodiesel reactor. In order to explore the possibility of using biodiesel as an additive, experimentation was carried out using four ball wear test machine (DUCOM Made). Results were obtained in the form of wear scar diameter (WSD) in microns and were recorded with the help of a microscope. Fig. 7 shows the WSD of Pongamia, Jatropha, Mahua and

Coconut oil methyl ester with conventional lubrication oil (SAE 20W40). A very good improvement in lubricity of lubricating oil i.e. decrease in WSD was observed with addition of biodiesel (0.5% only). Thus, it is clear that when this biodiesel is added in commercial lubricant, in small amount, lubricity gets improved. It was also noticed that addition of biodiesel in lubricating oil not only reduces the wear scar but also the coefficient of friction. Thus, addition of biodiesel imparts the lubricity to the final blend. Hence, biodiesel acts as a good lubricity improver and its market potential can be augmented by exploring its suitability as an additive to conventional lubricating oils and low sulphur diesel fuels.

6. Summary and discussion

This section describes the summary of the review done on the different biodiesel properties and engine system compatibility issues.

6.1. Cold fluidity of biodiesel

The cold flow behaviour of biodiesel greatly depends on the production procedure, reactants and reaction conditions and on the compositional structure of feedstock used. A reduction in saturated fatty acids reduces the ignition quality of the biodiesel, while an increase in unsaturation reduces oxidation stability. The cold weather performance of biodiesel assured that the length of the hydrocarbon chains and the presence of unsaturated structures noticeably influences the low temperature flow properties of biodiesel. High viscosity also causes numerous troubles in cold weather, as viscosity increases with decreasing temperature. Cold flow properties of biodiesel can be upgraded by thermal cracking and the alkoxylation method. Additive treatment with biodiesel is highly necessitated to realize the dream of using biodiesel in cold weather. Ozonization showed significant improvement in low temperature properties of biodiesel when biodiesel and additive were
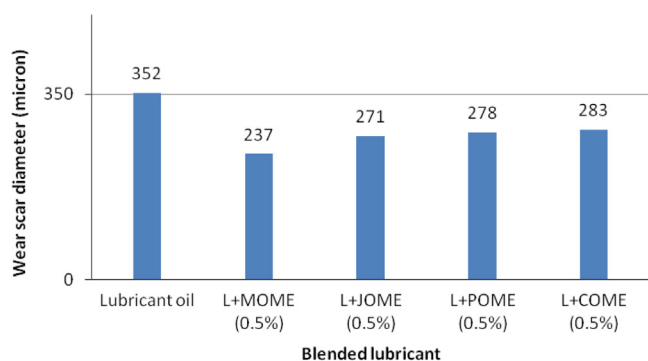
Fig. 7. Wear scar diameter of biodiesel blends with lubricating oil.

prepared from the same vegetable oil. Similarly winterization technique revealed significant enhancement in cold flow properties of biodiesel, but it results in lower yields, making this technique less acceptable.

Moreover, blending biodiesel with biodiesel was found to be the best renewable based technique to improve the cold flow properties and oxidation stability of the prepared binary blend. Again this technique is limited because it is predominantly applicable to the biodiesel produced from certain feedstocks only. Blending with fossil diesel is only effective at lower biodiesel proportions (up to 30 vol%) with cloud points to around − 10 °C. Clearly, blends with diesel do not change the chemical nature and therefore the properties of biodiesel and this will not facilitate its use at higher concentrations. Summary of cold flow behaviour of biodiesel, its effects, methods and improvement in cold fluidity is shown in Fig. 8 (Phase – I).

The consequence of some additives appears to be limited because they more strongly affect the pour point than more strongly the cloud point or they had only a slight influence on cloud point. The cloud point, however, is more important than the pour point for improving low temperature flow characteristics. Moreover, biodiesel is more prone to the solvency effect when stored at low temperature leading to the formation of precipitate which causes serious implications for the fuel carrying system. Storage temperature, storage time, biodiesel blend level, and feedstock affect the mass of precipitate formed.

Table 5 shows the biodiesel specifications for selected characteristics. It is revealed that cold flow characteristics are based on national biodiesel specifications for each region and time lapse. This suggests that the standard limit for cold flow properties of biodiesel is not globally same like other biodiesel specifications. Due to this, cold flow improving techniques need to be resettled as per geographic areas and their lowest temperatures.

6.2. Oxidation stability

Oxidation stability of biodiesel is a very complex process that is influenced by a variety of factors, including the composition of the fuel itself and conditions of storage. The different unsaturated components of biodiesel can generate different degradation products. Oxidation of biodiesel cannot be prevented totally but can be substantially slowed down by the use of antioxidants, which are chemicals that inhibit the oxidation process. Rancimat test (EN 14214, ASTM D6408-08, D5304-06) has been recommended as a significant method to determine the thermal stability of oils, fats and biodiesel fuels. ASTM D6751-05 indicates that the induction period should not be less than 3 h while EN 14214 requires a minimum of 6 h as determined by the Rancimat apparatus at 110 °C as shown in Table 5. Storage of biodiesel over extended periods may initiate degradation of fuel characteristics that can

compromise fuel quality. Hence, resistance to oxidative degradation during storage is an increasingly vital topic for the rapid development and feasibility of alternative fuels.

To obtain a very stable biodiesel and to avoid oxidation, it is needed to take special safeguard during the storage such as limiting access to oxygen and contact to light and moisture. Researchers found that water content and air exposure are two important factors affecting the degradation of biodiesel. The metal contaminated oxidation study revealed that, even a small concentration of transition metals showed the strongest detrimental and catalytic effect. Antioxidants are costly chemicals, hence, to avoid cost implications, metal deactivators can be used in order to meet oxidation stability as per standard. Also binary blends of antioxidants showed improved oxidation stability of biodiesel. However, the addition of antioxidants does not influence the diesel engine performance and emission. Efficiency of antioxidants varied depending upon the different types and quality of biodiesel and its blends with diesel and low sulphur diesel. Summary of oxidation stability of biodiesel, its effects on the engine system, methods and improving techniques is shown in Fig. 8 (Phase II).

The oxidation stability and the CFPP of the blended biodiesel had a close relationship with the fatty acid compositions. The oxidation stability of biodiesel decreased as the content of the linoleic and linolenic acids increased. The CFPP decreased as the unsaturated fatty acid content increased. When the biodiesel compositions are determined, their oxidation stability and CFPP can be easily predicted from correlations.

The consequence of oxidation stability can be measured by accounting antioxidant concentration, fatty acids and total glycerine content. It was further noted that the formation of insoluble compound can also be noticeably decreased by increasing relative antioxidant content and increased by total glycerine content. It was clarified that the supercritical methanol method is helpful, especially for oils/fats that have higher peroxide values. It was found that stability increases on increasing the dosage of antioxidants.

Antioxidants inhibit the formation of free fatty acids in triglycerides; the effect of this inhibition on significant fuel properties of biodiesel was studied. Biodiesel, due to higher flash point is considered as a safety fuel. However, biodiesel has double bond and also easily produces the peroxides; so might be considered to have provability of cause fire during storage/transport/handling. Hence, more study should be devoted towards considering the hazard possibility of biodiesel to regard it as the future fuel.

Future work is required regarding the comprehensive probe on the impact of diesel fuel composition on the stability of the finished blends, a more in depth evaluation of biodiesel chemical structure on the oxidation stability and the effect of various synthetic antioxidant additives on the oxidation behaviour of diesel/biodiesel blends.

6.3. Corrosive and acidic nature of biodiesel

Review on corrosion studies reported that biodiesel is more corrosive than diesel. However, there is no definite indication as to whether the degree of corrosion observed in biodiesel is within limits acceptable for automotive components. The corrosive nature of biodiesel increases with the concentration of biodiesel in the blend and the level of oxidation. Copper alloys are more prone to corrosion than ferrous alloys and aluminium alloys. Lead alloy coating on terne steel sheet, which is applied for automotive fuel tanks, is severely affected by biodiesel. Due to the presence of impurities and water, the corrosive nature of biodiesel increases. Formation of acid may result into fuel system corrosion. Literature revealed that hydroperoxides are very unstable product and have tendency to attack elastomer in negative manner. Summary of
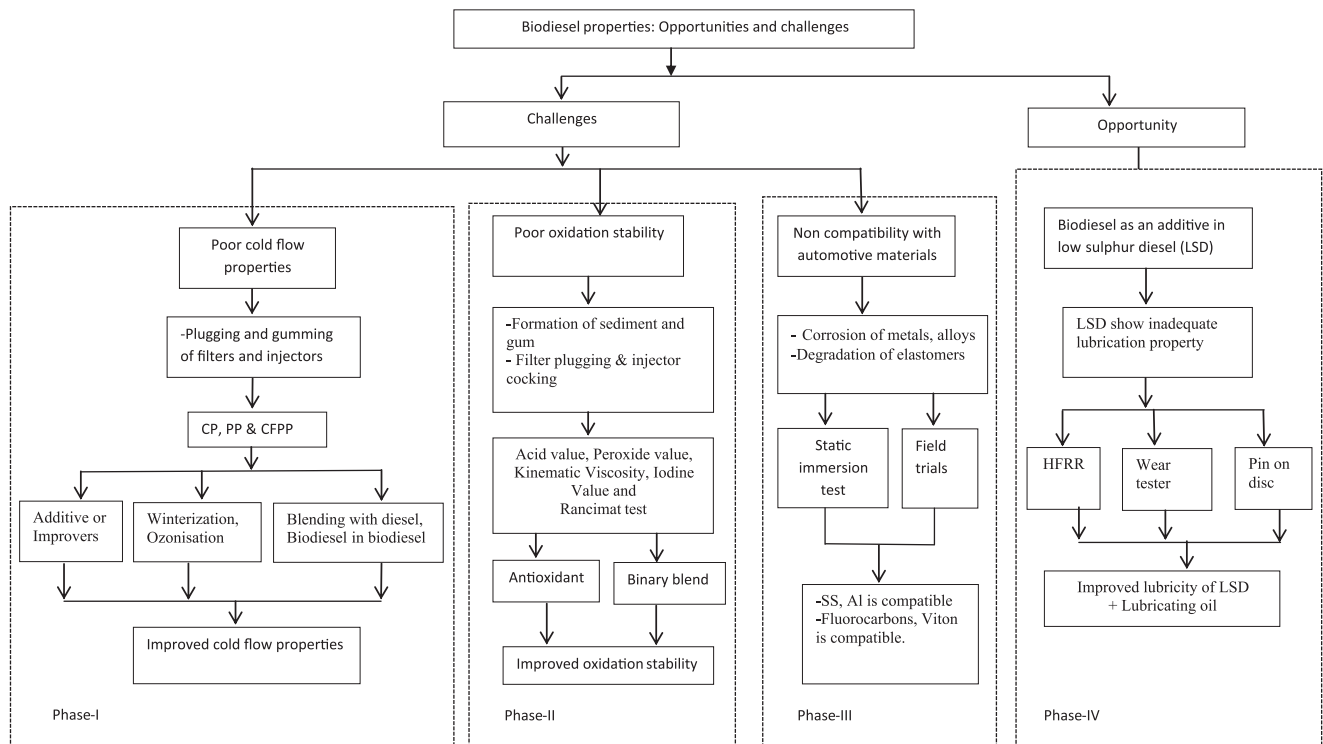
Fig. 8. Block diagram showing the challenges and opportunities in biodiesel properties in the context of automotive system compatibility.

Table 5
Biodiesel specifications.

SN	Characteristics	EU		US ASTM	
		Method	Limit	Method	Limit
1	Cloud point (°C)	EN ISO 23015	Based on National specifications	ASTM D2500	Report
2	Pour point (°C)	–	–	ASTM D97	Report
3	Cold filter plugging point (°C)	EN 116	Based on National Specifications	ASTM D6371	Report
4	Oxidation stability	EN ISO 14112	6 h min	EN ISO 14112	3 h min
5	Copper strip corrosion (3 h @ 50 °C)	EN ISO 2160	Class 1	ASTM D130	Class 3
6	Lubricity by HFRR	–	–	ASTM D6079	460 µm

compatibility of biodiesel with fuel system materials, its effects, methods and results is shown in Fig. 8 (Phase-III). Exact mechanisms of degradation of elastomers in biodiesel and the effects of different biodiesel constituents need methodical research.

6.4. Lubricity of biodiesel

It was investigated in literature that unrefined biodiesel showed higher lubricity property than refined biodiesels. In addition, methyl esters and monoglycerides are the main components that determine the lubricity of biodiesel but free fatty acids (FFAs) and diglycerides affected them slightly while triglycerides almost had no effects. By different methods, the lubricity of bio-based fuels achieved after the transesterification (alcoholysis) or pyrolysis of soybean oil are better than either of low sulphur diesel or high sulphur diesel. It is also remarkable to note that the use of pyrolysis products has a couple of potential advantages, being the biggest advantage the fact that there is no necessity for a large quantity of alcohol and respectively no production of waste glycerol.

The experimental investigation showed that addition of the esters consistently reduced the surface roughness values, even by as much as twofold compared to fuel oil. Furthermore, deformation on the surface studied by HFRR decreases with increasing the

concentration of biodiesel. Further, it is revealed that friction and wear is increased with increasing temperature. This may be attributed to the decreasing viscosity with increasing temperature. At higher temperature, lubricity enhancing film loses its permanence due to reduced viscosity and thereby increases wear. Also, higher blend tends to lower coefficient of friction. Summary of biodiesel as an additive in LSD and its measurement methods are shown in Fig. 8 (Phase-IV).

Fatty acids with longer carbon chain show superior lubricity property. Unsaturated fatty acids showed superior lubricity than saturated acids. However, according to Geller and Goodrum [144], the cause for lubricity performance of fatty acid esters was due to the exclusive structure of fatty acid methyl esters which aided the formation of hydrogen complexes. These complexes augmented the lubricity of mixtures containing these fatty acids esters.

The oxygen containing compounds and the mixtures of several fatty acids in methyl esters exhibits the best tribological ability to protect the sliding surfaces in fuel injection equipment. The presence of oxygen may accelerate the generation of inorganic oxides, like Fe_3O_4, which would have positive role in the formation of lubrication film at the contact interface. Moreover, results revealed that all the types of oxygen and nitrogen containing additives augment the lubricity of low sulphur diesel fuel. Available

literature revealed that lubrication mechanism of additives may depend on the constituents present and their polar constituent contribution. Furthermore, the branched chain ethers may facilitate in the growth of bio-based material for the probable use as an additive to improve various parameters of biodiesel such as lubricity, cold flow and oxidation stability. Besides, some studies revealed that alcohols appeared to be better lubricants than ethers at high concentration, may be due to their more pronounced polar nature. Literature showed that biodiesel provides better lubricity by reducing wear and friction. Conversely, biodiesel is more corrosive than fossil diesel which requires further comprehensive research to investigate tribo-corrosion through laboratory and field trials.

Out of various methyl esters reported, Coriander (*Coriandrum sativum* L.) seed oil methyl esters (CSME) have excellent fuel properties. CSME was prepared and evaluated by Moser and Vaughn [145] as an alternative biodiesel fuel and contained an unusual fatty acid, till now unreported, as the principle component in biodiesel fuels. The obtained Cetane number, kinematic viscosity and oxidative stability (the Rancimat method) of CSME was 53.3, 4.21 mm^2 s^{-1} (40 °C) and 14.6 h (110 °C). The cold filter plugging and pour points were −15 °C and −19 °C, respectively. Other properties such as acid value, free and total glycerol content, iodine value, as well as sulphur and phosphorous contents were acceptable according to the biodiesel standards ASTM D6751 and EN 14214. Also reported lubricity is the 167 μm wear scar. In brief, CSME has outstanding fuel properties as an effect of its unique fatty acid composition while accounting for lubricity, cold flow and storage stability. However, it has lower yield and higher cost; hence it can be used as an additive.

7. Conclusion

The review carried out on adverse biodiesel properties and its effect on engine system compatibility to discuss its long term acceptability issues in automotive application summarizes the following conclusion.

The literature results revealed that, the low-temperature flow inconvenience of bio-diesel can be improved by blending with petrodiesel, by winterization, by using additives, by developing branched-chain esters, or by adding bulky substitutes to the biodiesel molecules. It may be possible in the prospect to augment the necessary properties of biodiesel through genetic engineering of the feedstock oils, which could finally produce a fuel enriched with certain fatty acid(s), possibly oleic acid, which shows superior fuel properties. On this date, limited literature is available on low-temperature flow problem of bio-diesel, which needs further widespread and systematic research based on which strong decision for the usage of price competitive based biodiesel and its higher blend in cold weather could be made. At present, the field studies for biodiesel performance in cold weather are scarce.

The major aspects responsible for the oxidative processes of biodiesel are oxygen, metal traces, high temperature and the amount of unsaturated fatty acids. It was found that stability enhances on increasing the concentration of antioxidants. However, addition of antioxidant did not influence considerably the engine performance and emissions. The results obtained proposed that biodiesel fuel stored at lower temperatures is favourable for long time storage of biodiesel without degradation. The long-term storage stability study presents a better understanding of the influence of the different storage conditions on the stability of biodiesel. It is essential to take special safeguard during storage of biodiesel such as restricting access to oxygen and exposure to light, metal and moisture. Even if there are many investigations on storage, oxidation stability of biodiesel, and effects of antioxidants on the stability of biodiesel obtained from edible oils, less is

available on the oxidation stability of biodiesel from tree borne non-edible oil seeds and influence of the presence of metal on the oxidation stability of biodiesel from non-edible oil seeds.

Review of corrosion studies reported that biodiesel is more corrosive than diesel. However, there is no definite evidence as to whether the degree of corrosion observed in biodiesel is within limits acceptable for automotive components. With increase in the level of oxidation the corrosive nature of biodiesel increases. Copperish metals are more prone to corrosion than ferrous alloys and aluminium alloys. Due to the presence of impurities and water, the corrosive nature of biodiesel increased. Common elastomers like natural rubber, nitrile, chloroprene/neoprene, etc. are incompatible for use in biodiesel. Fluorocarbons have revealed good resistance and are suggested for use in biodiesel. Laboratory test data and field trial data available so far suggested that the metallic components made from ferrous alloys are perhaps compatible with lower blends of biodiesel. Right now, there are inadequate data available on corrosive behaviour, wear behaviour and elastomeric compatibility of CI engine fuel system materials in biodiesel and its higher blends which need further systematic and comprehensive research based on which confident decisions about the compatibility of materials could be made.

Literature indicated that biodiesel provides better lubricity by reducing wear and friction. Conversely, biodiesel is more corrosive than fossil diesel, which requires further comprehensive research to investigate tribo-corrosion through laboratory and field trials. Obviously, any additive treatment to biodiesel will need precise testing to verify the impact not only on the chemical and physical characteristics of the new formulated fuel, but its engine performance along with modest final unit cost of biodiesel. Moreover, there is a need to resolve systematically the unsolved challenges and opportunity issues due to biodiesel properties along with its effect on automotive system compatibility.

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